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Phosphorus recovery from source-separated urine
through the precipitation of struvite

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Contents

ABSTRACT	V
ZUSAMMENFASSUNG	VII
ACKNOWLEDGEMENTS	IX
CHAPTER 1.....	1
GENERAL INTRODUCTION	
CHAPTER 2.....	15
STRUVITE FORMATION	
CHAPTER 3.....	25
STRUVITE PRECIPITATION THERMODYNAMICS IN SOURCE-SEPARATED URINE	
CHAPTER 4.....	41
THE BEHAVIOUR OF PHARMACEUTICALS AND HEAVY METALS DURING STRUVITE PRECIPITATION IN URINE	
CHAPTER 5.....	59
STRUVITE PRECIPITATION FROM URINE - INFLUENCING FACTORS ON PARTICLE SIZE	
CHAPTER 6.....	75
DISCUSSION, CONCLUSION AND OUTLOOK	
Appendix 1	
THERMODYNAMICS OF STRUVITE PRECIPITATION IN SOURCE SEPARATED URINE	
<i>Conference Paper</i>	
CURRICULUM VITAE	101

Abstract

Background and Objectives

Domestic wastewater is built up of several components. One of the smallest components in terms of volume is urine, making up for less than 1% of the total wastewater stream. Despite this small volume, urine is a significant contributor of nutrients: it contains 85–90% nitrogen, 50–80% phosphorus, and 80–90% potassium excreted by humans. This aspect offers the opportunity to extract the nutrients and make them available for recovery and reuse. The project Novaquatis, within which this research was carried out, took up this opportunity as its starting point. NOVAQUATIS was a transdisciplinary research project concerned with urine source separation as a new element in wastewater management. In 2008, it won the “td-net award for transdisciplinary research” from the Swiss Academies of Arts and Sciences.

Aim of the thesis

This thesis focuses on the recovery of phosphorus from urine. It aims at providing insight into struvite precipitation as a method to sustainably remove phosphorus from urine. The main scientific contribution to wastewater treatment and phosphorus removal is threefold. First, it provides insights into the thermodynamic aspects of struvite precipitation and develops the necessary tools to conduct calculations within the complexity of the urine matrix. Second, it examines the fate of pharmaceuticals, hormones and heavy metals during struvite precipitation. Third, by assessing how process parameters affect phosphorus removal efficiency and crystal growth, it provides insights that will be of help for practical implementation.

Methodology

With urine diversion toilets (NoMix toilets) installed on the premises of EAWAG, urine was collected and stored. This urine was used for various batch and continuous experiments on lab scale. Also artificial urine was applied. Two different programs for chemical equilibrium modelling were applied to model different set-ups, to determine speciation and to estimate several parameters within the struvite separation system.

Thermodynamic Aspects of Struvite Precipitation

Struvite is a white crystalline powder, consisting of equimolar amounts of ammonium, magnesium and phosphate and 6 hydration molecules ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). It precipitates spontaneously in hydrolysed urine, which has an elevated pH of 9. Addition of magnesium causes struvite precipitation, leading to a phosphorus removal of up to 99 %. The solubility of struvite in urine was determined with laboratory experiments and thermodynamic modelling. For struvite in urine, a standard solubility product of $10^{-13.26 \pm 0.057}$ at 25 °C and a struvite formation enthalpy of 22.6 (± 1.1) kJ/mol was determined. As the ionic strength is high, special care has to be taken regarding the method to approximate the activity factor and the speciation. From our data, we identified that the Davies approximation with the two constants $A=0.509$ and $B=0.3$ agreed best with our laboratory results.

For practical purposes, a unique conditional solubility product $K_s^{\text{cond}} = [\text{Mg}_{\text{aq}}] \cdot [\text{NH}_4^+ + \text{NH}_3] \cdot [\text{P}_{\text{ortho}}] = 10^{-7.57} \text{ M}^3$ was derived to calculate struvite solubility in urine at 25 °C, pH = 9.0 and ionic strength $I = 0.4 \text{ M}$ directly from measured concentrations.

The fate of pharmaceuticals, hormones and heavy metals

If struvite is to be applied as a fertiliser product in agriculture, detailed knowledge is needed on the risk of introducing micropollutants from urine into the food production stream. In order to test the uptake potential, urine was spiked with hormones and non-ionic, acidic and basic pharmaceuticals. Hormones and pharmaceuticals remain in solution for more than 98%. Compared to applying urine directly, struvite as a phosphate recovery product from human urine can significantly reduce the hazard potential of pharmaceuticals and estrogens.

Although the daily intake of heavy metals per person is limited, some metals can be measured in the urine produced at the sampling location. However, heavy metals in struvite precipitated from normal stored urine could not be detected. Thermodynamic modelling revealed low or very low equilibrium solute concentrations for cadmium, cobalt, chromium, copper, nickel and lead. Experiments confirmed cadmium, copper and lead carbonate and hydroxide precipitation upon metal addition in stored urine. Most of the metals present in urine will precipitate in the storage tank due to the hydrolysis taking place there. For all metals considered, the maximum specific metal concentrations per gram phosphate or nitrogen showed to be typically several orders of magnitudes lower in urine than in commercially available fertilisers and manure.

Optimisation of struvite particle size

In order to enable the recovery of phosphorus from urine on a larger scale, this thesis investigated the effect of varying the process parameters pH, temperature, stirrer type and filtration on phosphorus removal efficiency and average crystal size. Struvite crystallisation in a continuously fed and stirred tank reactor was also tested, and was shown to be a suitable technology to remove and reuse phosphorus from fully hydrolysed urine.

Struvite formation from hydrolysed urine starts with instantaneous spontaneous nucleation. The nuclei develop into crystals. Their size stays relatively limited due to the typical high pH conditions in hydrolysed urine (between 36 and 136 μm). The factors pH, temperature and mixing have an effect on the degree of supersaturation and therefore are of influence on average crystal size. Minimal solubility is between pH 9 and 10, where a crystal size of 92 μm is reached. Due to the negative effects for maximum phosphorus removal and recovery, dilution of urine with tap water should be avoided.

Conclusions and Outlook

Struvite precipitation was shown to be a robust and effective method to recover phosphorus from urine, a concentrated wastewater stream. The product does not form a hazard for public health with respect to heavy metals and micropollutants. Whether we can and are allowed to reuse the phosphorus recovered as struvite in the agricultural production chain remains an issue to be further investigated.

Zusammenfassung

Einleitung

Häusliches Abwasser ist aus mehreren Einzelkomponenten zusammengesetzt. Mit einem Anteil von weniger als 1 % stellt Urin eine der kleinsten Komponenten des gesamten Abwasservolumens dar. Trotz dieses geringen Volumens trägt Urin einen bedeutenden Anteil an Nährstoffen bei. So enthält Urin 85–90% des vom Menschen ausgeschiedenen Stickstoffs, 50–80% des Phosphors und 80–90% des Kaliums. Diese Gegebenheit stellt eine gute Möglichkeit dar, um Nährstoffe aus dem Abwasserstrom zu extrahieren und sie für die Rückgewinnung und Wiederverwendung verfügbar zu machen. Diese Möglichkeit war der Ausgangspunkt des Projektes Novaquatis, innerhalb dessen diese Forschungsarbeit durchgeführt wurde. Novaquatis ist ein transdisziplinäres Forschungsprojekt, welches sich mit der Urinseparierung als neues Element der Siedlungswasserwirtschaft beschäftigt.

Ziel der Arbeit

Der Fokus dieser Arbeit liegt auf der Rückgewinnung von Phosphor aus Urin. Zielsetzung ist die Bereitstellung von Erkenntnissen über die Ausfällung von Struvit, als eine Methode der nachhaltigen Entfernung von Phosphor aus Urin. Der wesentliche wissenschaftliche Beitrag zur Abwasserreinigung und zur Eliminierung von Phosphor kann in drei Bereiche aufgeteilt werden: Erstens werden Erkenntnisse zu thermodynamischen Aspekten der Fällung von Struvit aufgezeigt, und die notwendigen Werkzeuge zur genauen Berechnung innerhalb der komplexen Urin-Matrix entwickelt.

Zweitens werden die Rückstände von Arzneimitteln, Hormonen und Schwermetallen während der Fällung von Struvit untersucht. Drittens werden durch die Beurteilung der Einflüsse von Prozessparametern auf die Wirksamkeit der Phosphoreliminierung und des Kristallwachstums, Richtlinien für die praktische Anwendung bereitgestellt.

Methodik

Mit Hilfe von Urin separierenden Toiletten (NoMix toilets) in den Gebäuden der EAWAG wurde Urin gesammelt und gespeichert. Dieser Urin wurde für verschiedene Batch-Versuche und kontinuierliche Versuche im Labormaßstab verwendet. Chemische Gleichgewichtmodellierungen wurden durchgeführt, um verschiedene Messanordnungen zu modellieren, Komplexbildungen zu ermitteln und um einzelne Parameter innerhalb des Struvitausfällung abzuschätzen.

Thermodynamische Aspekte der Fällung von Struvit

Struvit ist ein weißes kristallines Pulver, bestehend aus äquimolaren Anteilen von Ammonium, Magnesium und Phosphat, sowie 6 Anteilen an Kristallwasser ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). In hydrolisiertem Urin fällt es bei Anwesenheit von Ammonium und einem erhöhten pH-Wert von 9 spontan aus. Eine Zugabe von Magnesium führt zu einer Fällung von Struvit mit einer Phosphor Beseitigung von bis zu 99 %. Die Löslichkeit von Struvit in Urin wurde mittels Laborexperimenten und thermodynamischer Modellierung ermittelt. Für Struvit in Urin wurden ein Löslichkeitsprodukt von $10^{-13.26 \pm 0.057}$ bei 25 °C und eine Bildungsenthalpie von $22.6(\pm 1.1)$ kJ / mol ermittelt. Aufgrund der hohen Ionenstärke muss besonderes Augenmerk auf die Methodik gelegt werden, um den Aktivitätsfaktor und die Artenbildung anzunähern. Basierend auf unserer Datenlage konnten wir die Davies-Approximation

mit den zwei Konstanten $A=0.509$ und $B=0.3$ als beste Anpassung an unsere Laborergebnisse identifizieren.

Für die praktische Anwendung wurde ein eindeutig bedingtes Löslichkeitsprodukt $K_s^{\text{cond}} = [\text{Mg}_{\text{aq}}] \cdot [\text{NH}_4^+ + \text{NH}_3] \cdot [\text{P}_{\text{ortho}}] = 10^{-7.57} \text{ M}^3$ direkt aus den gemessenen Konzentrationen abgeleitet, um die Löslichkeit von Struvit in Urin bei einer Temperatur von 25°C, einem pH-Wert von 9 und einer Ionenstärke von $I = 0.4 \text{ M}$ zu berechnen.

Der Verbleib von Arzneimitteln, Hormonen und Schwermetallen

Für den Fall der Wiederverwendung von Struvit als Düngemittel für die Landwirtschaft wurde das Risiko einer Zuführung von Mikroverunreinigungen aus Urin in die Nahrungskette untersucht. Urin wurde angereichert mit Hormonen und nichtionischen, sauren und basischen Arzneimitteln: Hormone und Arzneimittel verbleiben zu mehr als 98% in Lösung. Struvit als ein Produkt zur Phosphatrückgewinnung aus menschlichem Urin kann erheblich das Gefahrenpotential von Arzneimitteln und Östrogenen verringern. Obwohl die Aufnahme von Schwermetallen pro Person und Tag gering ist, können manche Metalle im Urin an der Probenentnahmestelle gemessen werden. Allerdings konnten keine Schwermetalle im Struvit produziert aus normal aufbewahrtm Urin nachgewiesen werden. Die thermodynamische Modellierung ergab geringe bis sehr geringe Lösungsgleichgewichte für Cadmium, Kobalt, Chrom, Kupfer, Nickel und Blei. Experimente bestätigten Carbonat und Hydroxid Niederschläge für Cadmium, Kupfer und Blei nach Zugabe der Metalle in aufbewahrtm Urin. Der größte Teil der im Urin vorhandenen Metalle fällt aufgrund der im Sammelbehälter stattfindenden Hydrolyse aus. Für Urin ist, im Falle aller betrachteten Metalle, die maximale spezifische Metallkonzentration pro Gramm Phosphat oder Stickstoff normalerweise mehrere Größenordnungen geringer als in handelsüblich erhältlichen Düngemitteln.

Prozessoptimierung

Um die Rückgewinnung von Phosphor aus Urin im größeren Maßstab zu ermöglichen wurden in dieser Arbeit die Effekte veränderter Prozessparameter wie pH-Wert, Temperatur, Filtration und Rührertyp auf die Phosphorabtrennleistung und mittlere Kristallgröße untersucht. Es konnte gezeigt werden, dass die Kristallisation von Struvit in einem Ausschwemmreaktor eine geeignete Technologie darstellt, um Phosphor aus vollständig hydrolysiertem Urin zu entfernen und wiederzuverwenden.

Generell ist die Struvitkristallisation spontan und unmittelbar. Die Kristallisationskeime entwickeln sich zu relativ homogenen und kleinen Kristallen (36 - 136µm), was vor allem auf die hohen pH-Werte in hydrolysiertem Urin zurückzuführen ist. Faktoren, die die mittlere Kristallgröße beeinflussen sind vor allem diejenigen, die einen Effekt auf den Übersättigungsgrad von Struvit haben. Minimale Löslichkeit wurde zwischen pH 9 und 10 festgestellt, wo eine Partikelgröße von 92 µm gefunden wurde. Die Verdünnung von Urin mit Trinkwasser soll unbedingt vermieden werden, da diese damit die maximale Phosphorrückgewinnung verringern würde.

Schlussfolgerungen

Es konnte gezeigt werden, dass die Fällung mit Struvit eine robuste und effektive Methode darstellt, um Phosphor aus einem konzentrierten Abwasserstrom zurückzugewinnen. Ob der als Struvit zurückgewonnenene Phosphor in der landwirtschaftlichen Produktionskette wiederverwendet werden kann und darf, bleibt eine Frage weiterer Untersuchungen.

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“Do one thing, every day, that scares you”, Eleanor Roosevelt

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Mariska Ronteltap

Den Haag, 16 November 2008

General introduction

1.1 The element phosphorus

Phosphorus is essential for all life. For humans and animals, it is a major building block in DNA, in nerve cells, brain, bones and teeth. Phosphorus is also an important mineral macronutrient. Additionally, it plays a key role in energy management within the cells of flora and fauna: the conversion of the phosphorus containing ATP to ADP is the source of energy in most biochemical reactions. Together with nitrogen and potassium, it forms the main component of fertiliser products. Due to its limited natural availability, phosphorus is often the nutrient limiting biological productivity.

The element phosphorus (P), with an atomic weight of 30.97 g.mol^{-1} , is the fifteenth element in the periodic table. It has four allotropes: white, red, black and brown P. Phosphorus was discovered by Hennig Brandt in 1669, while he was distilling urine on his search for the philosopher's stone. The name comes from the Greek *phosphorus*, meaning light-bearing: the white form has the capacity to luminesce in air (Bryant, 2004). Due to its reactivity, phosphorus is seldom found as a free element in the natural world. In most natural systems phosphorus occurs in the +5 oxidation state, in the form of orthophosphates, polyphosphates, organophosphates and particulate phosphates.

1.2 Phosphorus cycle

The element phosphorus is contained in phosphorus ore deposits all over the world. Yet, the only significant global resource of phosphorus, rock phosphate, is concentrated in a limited number of places. Rock phosphate is a general term for rock that contains a high concentration of phosphate minerals, commonly belonging to the apatite group (Valsami-Jones, 2004). In the natural environment, the phosphorus cycle starts with the release of phosphate minerals through rock weathering. Through the process of erosion, inorganic phosphate moves to soil and rivers, where it is absorbed by plants and incorporated into organic molecules such as ATP or phospholipids. By ingestion phosphorus travels up the food chain. It is returned to the environment in the form of excreta and broken down cell tissue. Through wash-out it ends up in sediments of rivers and eventually oceans (Figure 1-1). This cycle takes 10^7 - 10^8 years before the deposits are transformed into phosphate rock and brought back to the surface. Phosphate mineral rock is therefore regarded as a non-renewable and limited resource. Considering its indispensability for food production and therefore human life, it is essential that we look for sustainable phosphorus recovery methods.

Since the discovery of phosphate rock mining in the second half of the 19th century, the introduction of phosphorus into the environment took on a much higher rate (Driver *et al.*, 1999). Of all mined phosphate rock, around 80% is used for the production of agricultural fertiliser. Other uses are detergents (12%), animal feeds (5%) and special industrial applications such as flame retardants (3%) (Steén and Steen, 1998). In the past, ground rock phosphate was used directly as a phosphorus source for agriculture. However, the availability of phosphorus from phosphate rock to plants is limited. To meet the total phosphorus demand of the plants, more material was needed. High transportation costs and increasing mining costs led to the use of rock phosphate for artificial fertiliser manufacturing.

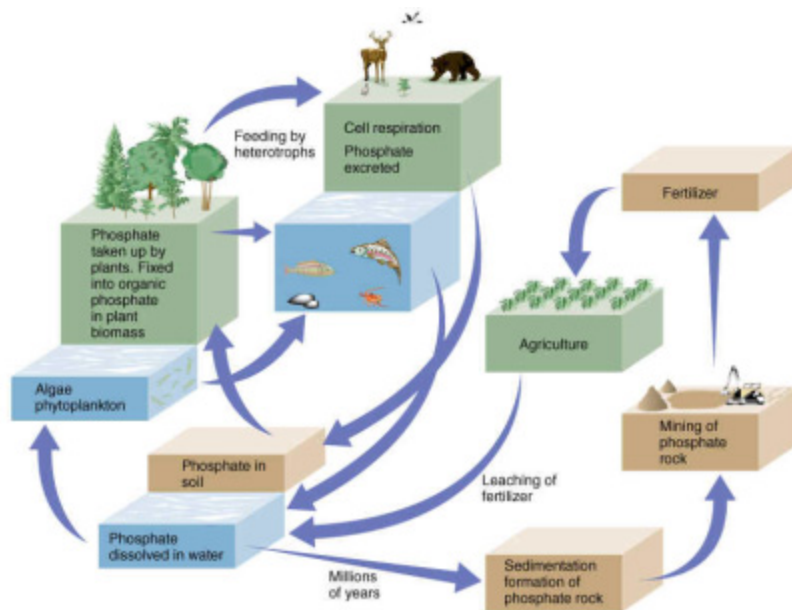


Figure 1-1. The cycle of phosphorus (Carosella, 2007).

The United States is the world's leading producer and consumer of phosphate rock (USGS, 2007). Other large sedimentary deposits are found in northern Africa, China and the Middle East. Large phosphate resources have been identified on the continental shelves and on seamounts in the Atlantic Ocean and the Pacific Ocean, but these cannot be recovered economically with the current technology (USGS, 2007).

Beginning in late 2007 and continuing into 2008, the price of phosphate rock jumped dramatically worldwide owing to increased agricultural demand and tight supplies of phosphate rock. The average U.S. price was more than double that of 2007, approaching \$500 per ton. Prices for nitrogen, potash, and sulphur also increased, thus causing the price of fertilisers to reach record highs (U.S. Geological Survey, Mineral Commodity Summaries, January 2009).

There are several developments contributing to the increasing pressure on the phosphate reserves. First of all, the world population keeps growing. The United Nations has estimated that by year 2050, the global population will have increased by a further 40% to reach 9 billion people (United Nations, 1999). Second: It is not only the number of people to be fed that grows; also the demand per person is growing. The economies of China and India increased substantially over the last years, increasing the middle income segment in the two largest countries of the world. Rising income leads to the demand for better and more extended food patterns. The combined effects of rising population and wealth will inevitably increase the demand for higher dietary standards and higher-grade foodstuffs, particularly meat and dairy products, the production of which is very grain-intensive. The cereals to meat conversion ratio in intensive animal husbandry is 3:1 for poultry, 4.5:1 for pork and 6:1 for red meat (Steén, 1998).

Cultivating the fertile soils is no longer sufficient; also land less suitable for agriculture needs to be cultivated to meet the demand. The preparation of less fertile land for cultivation requires a larger quantity of fertilisers. Recent developments in heavy rain falls and extended periods of draught related to the effects of climate change further limit the availability of fertile soils. Finally, the production of crops for non-fossil fuel production increases the use of fertiliser even more. The demand for crops for biofuel, primarily from corn, sugar and vegetable oils, has increased

substantially since the year 2000. The European directive on biofuels, which was adopted in 2003, sets recommended targets for biofuels as a share of the total fuels used for transport. The aim was to increase that share to 2% by the end of 2005 and to 5.75% by 2010. This will further increase the pressure on the available amount of fertilisers. The conflict for arable land is also known as the food, feed and fuel competition. Current estimates state that if our global consumption annually increases with 2.5 %, phosphorus might already be running out in ca. 60 years (Driver *et al.*, 1999). More generally, reserves are estimated between 1.2 to 5×10^{10} tonnes (Steén and Steen, 1998). Depending on the assumed scenario, this would be sufficient to provide us with phosphorus for a period of 50 to 300 years. Apart from quantity, an even greater worry is quality: high-grade ores with high P_2O_5 concentration and low on contaminants are being progressively depleted. Consequently, production costs will further increase (Steén, 2004).

1.3 Phosphorus: waste or resource? A historical perspective

As long as people lived together in relatively small groups, nature could break down their waste products without any problems. When people started to live close together in bigger settlements, their liquid and human waste became a burden. In ancient Rome, the waste was taken care of by water washing the streets clean into the sewer system, the *cloaca maxima*, constructed around 600 BC. During the process of urbanisation in the second half of the 19th century the amount of human waste within the city limits became problematically large and led to problems with public health. In the Netherlands an initial solution was provided in the form of the Boldoot cart (Henze *et al.*, 2008). Human waste was collected with buckets and, analogue to animal wastes which have been known for centuries to be beneficial for the land, transported to agricultural fields. In several cities this was replaced by a system of vacuum sewers, sucked empty by the Liernur vacuum pump truck (Figure 1-2). It was calculated that the cities could make a profit of one guilder per person per year through the sales of “humanure” to the farmers (Van den Noort, 2003).



Figure 1-2. Collection of human waste in Amsterdam in the 1950s by the so-called Boldoot system (Boldoot was the name of an eau de cologne that was popular in those days) (left); the Liernur vacuum system to empty the first sewers (right) (Van den Noort, 2003).

With the construction of the first wastewater treatment plants in the first decade of the 20th century, the wastewater no longer found its way back to the agricultural fields, but was channelled to the wastewater treatment plants (Henze *et al.*, 2008). Although the upcoming of the municipal wastewater treatment plants offered much improvement in terms of removal of organic pollutions - with respect to nutrients a new problem was created. The early versions of wastewater treatment did not comprise of nutrient removal schemes, and phosphorus and nitrogen derived from human

waste ended up in local high concentrations in receiving water bodies. This process of discharging the nutrient-rich effluent into sensitive water bodies led to eutrophication. Eutrophication can be defined as the enrichment of waters by nutrients and the resulting deterioration of quality due to the luxuriant growth of plant life and its resultant effect on the ecological balance of the affected waters. With the implementation of the EU Urban Waste Water Treatment Directive 91/271, phosphorus removal became obligatory for all treatment plants treating the wastewater of 10,000 or more person equivalent and discharging into water bodies susceptible to eutrophication. This legislation formed an extra incentive for the development of phosphorus removal techniques.

Phosphorus removal from wastewater implies the transformation of dissolved phosphorus to a solid phase, typically sludge. For a long time, the phosphorus-rich sludge was transported from the wastewater treatment plant to the agricultural plots, and the nutrient cycle - be it more extended – remained more or less intact. However, for a number of reasons independent from phosphorus contents, agricultural re-use of sewage biosolids is diminishing throughout Europe (Lijmbach, 2002). This break in the nutrient cycle is twofold problematic. First, it means that on phosphorus needs to be mined more intensively. With phosphate rock being a finite resource, this is an unsustainable practice. Second, another pathway to dispose of the biosolids has to be found. Typically this is done by incineration, where phosphorus ends up as sludge incineration ash in a landfill (Lijmbach, 2002).

To reach a more sustainable situation, phosphate from waste streams should to be recovered rather than being disposed of. Making use of recycling or reuse processes is not only good practise from an environmental and sustainability point of view. Due to the current price developments for raw phosphate rock, recycling also becomes essential from an economical viewpoint. The recovery of phosphate for recycling can be done at several locations within the wastewater treatment process. The recovered phosphorus can become a recycling product within the phosphate industry.

1.4 Phosphorus removal from wastewater

The wastewater treatment industry presently uses several methods to remove phosphorus. All of these technologies are based on the principle of converting the aqueous phosphorus ions into a solid fraction (De-Bashan and Bashan, 2004). Physico-chemical phosphorus removal leads to the formation of an insoluble salt precipitate. Via biological phosphorus removal, phosphorus ends up in a microbial mass in an activated sludge, or plant biomass in constructed wetlands.

1.4.1 Physico-chemical phosphorus removal

For chemical precipitation of phosphorus di- or trivalent metal salts can be added. The metals form poorly soluble phosphates, which settle in the designated sedimentation area. Typically iron(II), iron(III) or aluminium(III) is added, with chlorides and sulphates as counter ion. For the precipitation of calcium phosphates lime can be used. Often, anionic polymers are added to enhance solid separation after the phosphate is formed (Morse, 1997).

Typically, jar tests are performed to determine the most efficient salt and its optimal dosing to precipitate the phosphorus in a certain wastewater. Not so much the phosphorus concentration determine optimal dosing but rather other factors, such as pH value, alkalinity and other ionic constituents present in the wastewater.

Within the treatment plant, several locations can be employed for the metal salt dosing. This is categorized into primary, secondary and tertiary chemical phosphorus precipitation (Figure 1-3). Primary treatment is based on the addition of a metal salt to the wastewater prior to the first sedimentation tank. The phosphate is then removed together with the primary sludge. Typical for this procedure is the removal of at least double the amount of BOD that would normally be removed in this step. In secondary precipitation, the salt is added immediately prior to aeration. Because bio-flocculation of the chemical precipitates occurs, also colloidal or fine precipitates can be removed. This enables the use of cheaper chemicals in lower dosing. It has the disadvantage of producing up to 30% more sludge. Tertiary precipitation describes the system where the salts are added either directly before the secondary clarifier, or directly after that, which would require a tertiary solid liquid separation step. In general, 70-95% phosphorus removal can be expected with chemical phosphorus removal.

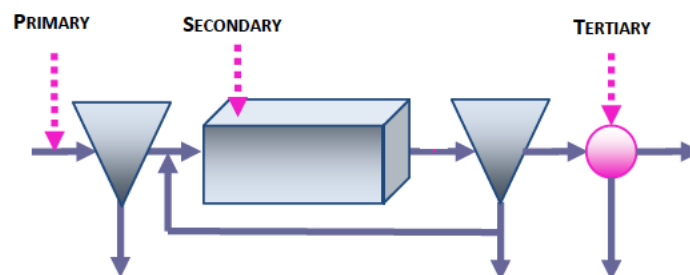


Figure 1-3. Possible metal salt addition points in a wastewater treatment plant, making the precipitation primary, secondary or tertiary of nature (information: Parsons and Berry, 2004).

Besides the costs of chemicals, which are generally low, the main disadvantage of chemical phosphorus removal is the production of extra sludge. This can range from a 50% up to a 150% increase compared to a system without P-removal (Parsons and Berry, 2004). The disposal of sludge currently costs €65 – 90 per tonne for Dutch water boards (Harm Baten, *Water Board Stichtse Rijnlanden, pers. comm.*, 2009). Parsons and Berry (2004) summarize the direct drawbacks of chemical phosphorus removal as:

- Side reactions take place: the metals react with the alkalinity to form poorly soluble metal hydroxides, accompanied by a pH reduction
- The residual coagulants have negative effects on nitrification, leading to elevated effluent concentrations in ammonium
- The corrosiveness of the metal salts shortens the life span of the treatment plant's hardware
- Sludge production increases while at the same time the dewaterability of the sludge decreases.

1.4.2 Biological phosphorus removal

Another route to remove phosphorus from wastewater is by making use of the phosphate accumulating ability by a selected group of microorganisms, phosphate accumulating organisms (PAOs). After its accidental discovery in the 1950s, this ability has been studied in detail and applied in a technique called enhanced biological phosphorus removal (EBPR). The EBPR process is based upon the exposure of activated sludge to initially carbon-rich, strictly anaerobic conditions, followed by carbon-poor, aerobic conditions. In the first anaerobic phase in the treatment plant, the release of dissolved P is accommodated for. The organic matter and carbon sources from the wastewater are metabolised and storage biopolymers are formed within the microorganisms. The energy for this

process is obtained from the hydrolysis of the internal energy source polyphosphate. This causes soluble orthophosphate to be released into the mixed liquor. In a subsequent aerobic phase, the storage biopolymers serve as energy and carbon sources for the phosphate accumulating bacteria to take up phosphate to assist in their energy household. More phosphate is taken up than was originally released, and it is stored intracellular in the form of polyphosphate. By separating the P-rich sludge from the cleaned effluent, the wastewater ends up phosphate-poor, and in case of complete EBPR success, phosphate-free. This technique leads to a substantial smaller sludge production than chemical phosphorus removal (Jardin and Pöpel, 1997). Yet, during sludge handling the phosphorus can be released again. Storage of waste activated sludge typically takes places under anaerobic conditions, which leads to the sludge releasing its phosphorus again. If the sludge is thickened quickly, the phosphorus remains with the sludge, but may then be released during sludge digestion (Strickland, 1999).

Both processes have their advantages and disadvantages. In comparison to biological removal, chemical phosphorus removal leads to a larger sludge production, which leads to higher costs for sludge treatment, disposal and final management (Janssen *et al.*, 2002). Moreover, the salinity of the effluent increases. On the offset, optimal biological phosphorus removal is dependent of the composition of the wastewater. Because of this, the system is more sensitive to changes and is therefore less stable. Additionally, a well-defined anaerobic stage has to be added to the treatment process to accommodate the phosphate accumulating organisms, PAOs (Janssen *et al.*, 2002).

From both pathways, phosphorus recovery can be implemented, for which different methods are available.

1.5 Phosphorus recovery from streams within the wastewater treatment process

Driven by an urge for sustainability and a progressive legislation in a number of countries in Europe, the interest for phosphorus recovery methods lead to the development of several techniques (Steén, 2004). There are several waste streams in the society that could form a source for P recovery.

- The ash of incinerated sludge can form a source of phosphorus available for recovery. The organic material is burnt, the inorganic remains, among which the phosphorus removed from the wastewater. Ash from bio-P sludge generally has a higher P-content than ash from chemical P precipitation sludge: 360 vs 190 g P_2O_5 /kg ash (Lijmbach *et al.*, 2002). They both typically contain too many metals (Fe, Cu, Zn) per gram P for it to be a useful source for the P industry (Klapwijk and Temmink, 2004). A two-step thermal treatment is suggested by Adam *et al.* (2009) to make the phosphorus better available to plants, and to separate the phosphorus from the heavy metals. The first step of mono-incineration completely destroys organic pollutants. In a second thermo-chemical step, P is transferred into mineral phases which are better available for plants. By providing a chloride donor, the heavy metals are transformed into volatile heavy metal chlorides, which evaporate. Yet, additional energy considerations were not taken into account in this study.
- Dissolved phosphorus released from waste activated sludge from a plant with biological phosphorus removal is an excellent source for phosphorus recovery (Gaterell, 2000). There are two main pathways to obtain a compact P-rich stream within the process of a biological phosphorus removal plant. First, P can be extracted from the P-rich sludge just before it enters the sludge treatment facilities. A process set-up that applies this procedure is the BCFS process,

a side-stream P precipitation process (Van Loosdrecht *et al.*, 1998). Mixed liquor is extracted from the first, anaerobic, compartment. The sludge is sedimented, leaving a P-rich supernatant. This supernatant can form the basis of a P recovery stream. Alternatively, phosphorus can be released from the return sludge in an anaerobic phase, after an aerobic P uptake phase and a sludge sedimentation step. The sludge is sedimented again after the P extraction, and also here a smaller P-rich side stream is obtained.

- A third method is to precipitate the phosphorus from the supernatant of the sludge after digestion. Prerequisite is that this sludge still contains the phosphorus from the wastewater, and not just intracellular P from biomass. Considering the reporting of spontaneous precipitation in this stream, conditions for precipitation are good (Borgerding, 1972).

To recover phosphorus from these P-rich streams, several methods are available. A few examples are ion exchange, adsorption or precipitation on bacteria surfaces or for example magnetism (Morse *et al.*, 1998). Yet, the most applied technique is crystallisation. The crystallisation process leads to the production of a phosphate crystal which can be re-introduced into the phosphorus industry depending on its characteristics. The two common products in P-recovery process are magnesium ammonium phosphate, MgNH_4PO_4 (MAP or struvite) and calcium phosphate compounds ($\text{Ca}_x(\text{PO}_4)_y$). Each of these forms are being produced in pilot or full scale reactors, for example the DHV Crystallactor® process producing calcium phosphate pellets or the CSIR fluidised bed crystallisation forming either hydroxylapatite or struvite depending on the constituents of the feed stream (Steén, 2004). In Japan, struvite precipitation from digester supernatant after dewatering is taking place at Shimane Prefecture Sewage Works (Ueno and Fujii, 2001). Calcium phosphates are generally precipitated on seeding material such as sand; struvite often forms spontaneously.

Summarizing, there are different recovery techniques possible for phosphorus from wastewater streams. Crystallisation is the most widely applied technique typically forming magnesium or calcium phosphates, from preferably concentrated streams.

Next to the phosphorus rich streams evolving from conventional wastewater treatment, there are other waste streams suitable for phosphorus recovery processes. In domestic wastewater, this stream is human urine. Compared to the typical phosphorus concentrations in the P-rich streams from wastewater treatment, human urine offers a more concentrated stream. In the next paragraph the rationale behind the separation of human urine is described in detail.

1.6 New developments in the urban wastewater cycle: No-Mix technology

So far, the system of wastewater collection through sewers and the subsequent treatment in wastewater treatment plants has served us relatively well with respect to the two goals of sanitation provision: protect public health and the natural environment.

However, the sewer systems in Europe are reaching respectable ages (Sørensen *et al.*, 2006; Buiters, 2005; Gandy, 1999), and revisions become inevitable. Considering the amount of money involved in the rehabilitation process - Burkhard and González Lakehal (2006) indicated a rehabilitation price of €30,000 per kilometre of sewer, leading to €30 million for the city of Zurich alone - this is a good moment have a critical look at our current wastewater system.

A method that can offer many benefits is the separation of different waste streams at the source. The waste streams building up the total mixed wastewater stream each have different levels of

pollution and are generated in different quantities at different times. Keeping them separate from the beginning offers more flexibility and efficiency considering treatment and reuse.

With respect to source separation and separate treatment, urine forms one of the most interesting streams. Urine contains a large part of the nutrients in wastewater – about 80 % of the nitrogen and 50 % of the phosphorus –although urine itself accounts for less than 1 % of the total volume of wastewater. Urine separation can be carried out by applying so-called “NoMix technology”. This concept works as follows: urine is collected in the front compartment of specially designed toilets (for example Figure 1-4) and drained, with a little flushing water or even undiluted, into a local storage tank. Then this small but concentrated nutrient stream becomes available for specifically targeted removal or preferably recovery technologies.

This concept was studied in detail in Eawag’s award winning interdisciplinary research project NOVAQUATIS. From this project, it was concluded that separating urine from wastewater offers various advantages: because wastewater treatment plants now receive a much smaller nutrient load, their footprint can become much smaller, while at the same time water bodies could be more effectively protected from nitrogen and phosphorus inputs. Moreover, the nutrients become available for recycling. One of the major sources of concern for the current wastewater systems, its inability to remove endocrine disrupting micropollutants – hormones and pharmaceutical residues – can also be dealt with more specifically if urine is kept concentrated. Urine source separation can undoubtedly increase the flexibility of wastewater treatment (Larsen and Lienert, 2007).



Figure 1-4: A modern NoMix toilet (photo website Sealskin).

After urine is collected separately, it is available for specific treatment technologies. Several options are available:

- Urine can be used directly as a liquid fertiliser (Kirchmann *et al.*, 1995). Specific guidelines are available how to safely reuse urine as a fertiliser in agriculture (WHO, 2006). However, despite the possibility, direct reuse of urine is not widely applied in industrialised countries. This is mainly due to issues related to micropollutants contained in urine, a perceived hygiene risk, and an expected soil and plant sensitivity to the high salt concentrations (Maurer *et al.*, 2002).
- Once urine is collected with source separating systems, the existing sewer network could be used for transport to a treatment facility at night when the sewers are empty (Larsen and Gujer, 1996). Alternatively, trucks can be used for transport. The advantage of transporting urine to the treatment plant separate from the wastewater would be that large nutrient spills during combined sewer overflows can be limited. Additionally, the operator of the treatment plant has more control over the dosing of ammonia to the plant over the day. Urine can also be nitrified before transport in the sewers, and as such function as a smell reducing agent: the produced nitrate serves as an electron acceptor to prevent hydrogen sulphide production (Oosterhuis, 2007).
- The unique properties of urine mean that a wide variety of technologies may be used to treat it. Maurer *et al.* (2006) defined seven main purposes of a treatment unit: volume reduction, P-recovery, N-recovery, stabilisation, hygienisation, removal of micropollutants and biological

nutrient removal. For phosphorus recovery from urine, only struvite formation is mentioned in literature. Struvite formation in urine is a fast and relatively easy process: the addition of magnesium triggers the precipitation without any noticeable lag phase (Maurer *et al.*, 2006). Struvite can be applied as a slow release fertiliser, which makes it a useful recovery product that would enable a closing of the nutrient loop.

In this thesis, we apply the knowledge on struvite obtained from different fields to the recovery of phosphorus in the form of struvite from source separated urine. It aims to provide thermodynamic aspects of struvite precipitation, as well as the necessary tools to perform calculations within the complexity of the urine matrix. The results of this study are presented in Chapter 3. The applicability of the recovery product with respect to micropollutants needs to be studied and explained, which is done in Chapter 4. Finally, the thesis aims to offer more insight in particle size determining factors to aid implementation of struvite precipitation as a P-recovery method from source separated urine. This is presented in Chapter 5. Chapter 2 will first provide some more background information on struvite and the formation process.

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Struvite formation

A literature overview

2.1 General background

Struvite is a phosphate mineral, of the group of the orthophosphates. Struvite was first described when it was found in medieval sewer systems in Hamburg in 1845. It received its name from geographer and geologist Von Struve (1772-1851). Struvite is built up from magnesium, ammonium and phosphate in a molar 1:1:1 ratio, typically surrounded by six water molecules. This leads to a molecular weight of 245.41 gram per mol. The crystals have an orthorhombic structure of a PO_4^{3-} and $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ octahedral and NH_4^+ groups bound by hydrogen bonding (Abbona and Boistelle, 1979). Physically, struvite consists of a fine white powder which dissolves poorly in water ($0.018\text{g}\cdot 100\text{ ml}^{-1}$ in water of 25°C), yet more easily in acidic solutions ($0.178\text{g}\cdot 100\text{ ml}^{-1}$ at 25°C in 0.01 N hydrochloric acid; Bridger *et al.*, 1962).

Struvite however is also known as a problematic compound, particularly in wastewater treatment plants and sludge treatment facilities. Borgerding (1972) reported heavy scaling of struvite at the Hyperion treatment plant of Los Angeles, mainly on the walls of the anaerobic digestion system. Treatment with acid initially took care of the problem; yet, the problem returned, strongly reducing pipe diameters. Precipitation particularly occurs in curves and bends because of the local pH rise. Also in urine collecting systems, blocking pipes by struvite have been reported (Udert *et al.*, 2003a; Udert *et al.*, 2003b). Over the years, many treatment plants have dealt with this issue. Consequently, it was also the topic of study for many researchers.

Forced precipitation of struvite was originally investigated as a method to prevent problems in the operating system (Stratful *et al.*, 1999). Struvite precipitation from digester supernatant is already taking place on a larger scale: in Japan, three P-recovery units are operational at Shimane Prefecture Sewage Works, two of which have been in place since 1998 and one since 2000 (Ueno and Fujii, 2001). They deliver a feed concentration of $100\text{--}110\text{ mg P}\cdot\text{L}^{-1}$, and after addition of magnesium hydroxide and sodium hydroxide, struvite precipitates as pellets in a fluidized-bed reactor. The struvite pellets are free from contaminants, and are sold to fertiliser companies as raw material. Other phosphate industry plants however indicate they cannot adopt struvite in their phosphate producing processes (Schipper *et al.*, 2001). The nitrogen present in struvite would cause a serious emission or gas scrubbing problem in the sintering stage, since ammonium would be volatilised and oxidised to nitrous/nitric oxides. However, due to its composition, struvite itself is a valuable slow-release fertiliser. This aspect was recognised as early as 1857, and its fertiliser value has been emphasized repeatedly (Bridger *et al.*, 1962, Gaterell *et al.*, 2000, Johnston and Richards, 2003).

Struvite is found to be thermally instable in temperatures over 50°C (Sarkar, 1991). The ammonia and water molecules of struvite evaporate depending on the time and temperature of the heat treatment, ultimately forming magnesium hydrogen phosphate trihydrate ($\text{MgNPO}_4\cdot 3\text{H}_2\text{O}$). When struvite is further heated, monohydrate ($\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$) is formed. Iqbal *et al.* (2008) reported the thermal decomposition of struvite to be dependent of the rate of heating. Through gradual loss of ammonia and water molecules, struvite was found to be transformed into amorphous magnesium hydrogen phosphate (MgHPO_4). When struvite is heated in the presence of excess water, it is partially transformed into bobierite ($\text{Mg}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$), through the gradual loss of ammonia (Iqbal *et al.*, 2008).

Struvite formation, as any other crystal build-up, occurs by nucleation formation followed by crystal growth. In the next chapter this process is described in more detail.

2.2 Nucleation and crystal growth

The formation of crystals from aqueous species follows two chemical stages: first nucleation takes place, a process also referred to as crystal birth. Second, crystal growth sets in, where the crystals continue to grow until an equilibrium is achieved (Mullin, 1993).

Nucleation may occur spontaneously or may be induced by external factors such as temperature or agitation.

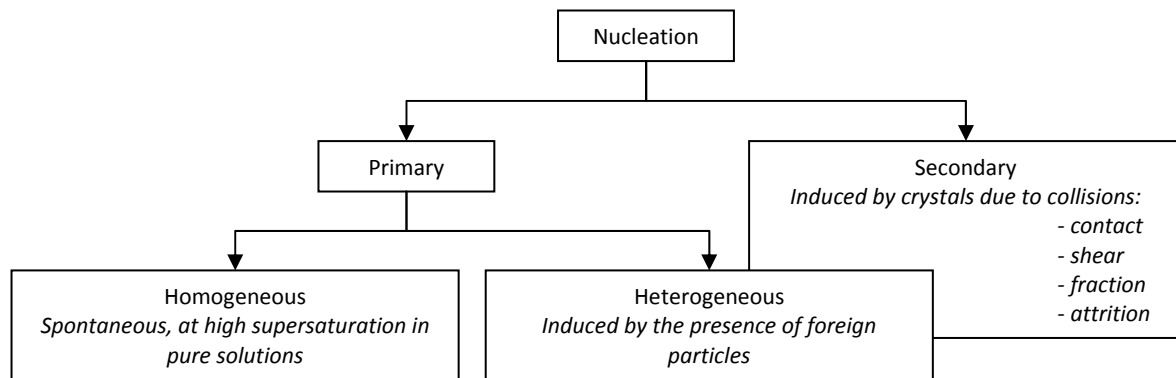


Figure 2-1: Diagram of possible nucleation processes (adapted from Mullin, 1993; Jones, 2002).

Nucleation can be primary or secondary. Secondary nucleation occurs at lower supersaturation levels, and is initiated by contact with a surface, for example already formed crystals, a mixer blade or a vessel wall (Mersmann, 1995). Primary nucleation occurs at higher supersaturation, and can be homogenous or heterogeneous. Homogenous nucleation describes the formation of crystals in a solution completely free from other particles or rough surfaces. Heterogeneous nucleation occurs when there are impurities within the system: foreign surfaces which decrease the free energy needed to form a critical nucleus (Mullin, 1993; Mersmann, 1995).

During crystal growth, nuclei grow out into crystals of visible size. The process is thought to be built up from two steps: a diffusion step of mass towards a boundary layer, and an integration step from the boundary layer to the surface (Mersmann, 1995). If the movement of mass towards the crystal surface is the rate limiting step, growth rate is considered to be diffusion-controlled. When the mechanism of incorporating mass into the crystal is rate controlling, we speak of integration-controlled growth (Mersmann, 1995). Temperature can be an influencing factor in determining the type of growth. Crystallisation at elevated temperatures usually leads to diffusion controlled growths, while surface integration controlled growth is more dominant at lower temperatures (Jones, 2002). Generally, growth rate expressions describe the growth of a crystal by the removal of mass from solution relative to time (Mullin, 1993). Several other physicochemical aspects were reported to have an effect on crystal nucleation, growth and morphology. These aspects will be discussed further in paragraph 2.4.

The time it takes until the first stable nucleus is formed is called the induction time. Bouropoulos and Koutsoukos (2000) demonstrated that the induction time was inversely proportional to the supersaturation level, making the supersaturation level one of the most influencing parameter on induction time (Le Corre, 2006).

2.3 Supersaturation

Supersaturation is a very important parameter in crystallisation processes. Saturation is the degree in which the solute concentration deviates from its equilibrium in a given solution. It is determined by the ratio of ion activity product and the solubility constant. For struvite, the degree of saturation S is defined as:

$$S = \frac{f_1(NH_4^+)f_2(Mg^{2+})f_1(PO_4^{3-})}{K_{s,0}}$$

where f represents the activity of the ionic species relative to the struvite components in solution and $K_{s,0}$ the struvite solubility product (see section 3.3.1 of this thesis). The activity of the ionic species depends on the valence of the ions as well as on the total ionic strength of the solution. Further details will follow in chapter 3.

A solution can, with respect to supersaturation, be in three different states (Jones, 2002; Mullins 1993; see Figure 2-2):

- **Undersaturated:** in this phase, the solubility of the solids is not exceeded and therefore crystal formation cannot occur.
- **Metastable:** in this state, the solution is oversaturated, but the free energy is still too low for spontaneous nucleation. In the solubility curve, this zone is indicated in between the solubility curve and the supersaturation curve.
- **Oversaturated:** the solute concentration exceeds the equilibrium value, and spontaneous nucleation can occur.

In order to overcome the supersaturation curve, (1): the solution can be cooled while preserving the concentrations, (2): the solvent can be concentrated by evaporation or solute addition at constant temperature or (3) these two methods can be combined.

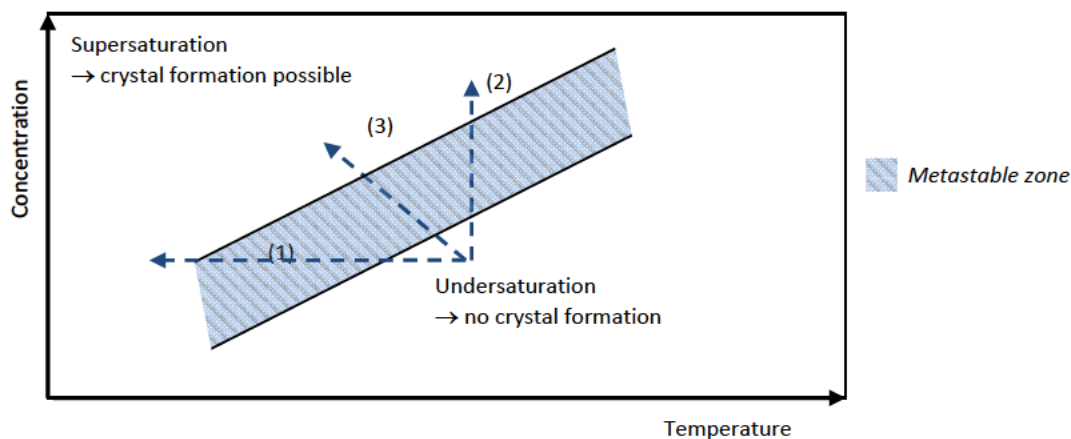


Figure 2-2: Possible solution states with respect to supersaturation (Jones, 2002, in Le Corre, 2006)

Abbona and Boistelle (1979) showed how struvite habit is variable and depending on growth conditions. Pure struvite crystals do not take one form, but can have different morphologies depending on the conditions under which they were grown. By growing crystals from pure solutions, the effect of supersaturation on different morphologies was shown: X-shaped crystals appear at high supersaturation, coffin lid-shaped crystals at lower supersaturation.

2.3.1 Impurities in the crystals

During the build-up of crystals, also foreign ions can become part of the crystal lattice. There are 3 main types of lattice imperfection: point, line or surface imperfection (Mullin, 1993). Point imperfections are caused by holes in the structure of the crystal, a typical phenomenon with larger molecules. Line imperfections are the consequence of dislocations: abnormalities during the formation of a crystal leading to connection sites for other molecules (Figure 2-3). Surface imperfections occur when a number of dislocation lines are formed next to each other; this can happen under mechanical or thermal stress. Figure 2-3 shows several locations where, apart from the same molecule, also foreign structures can bind.

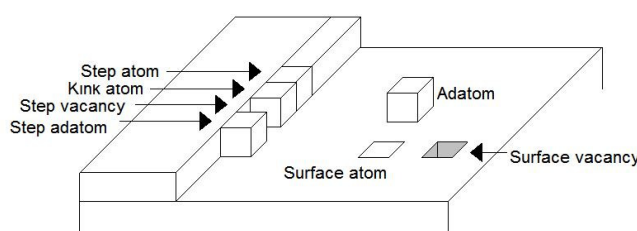


Figure 2-3: Model for crystal growth, showing several locations or kinks where newly formed molecules can attach to the lattice (Wikipedia, 2009; based on the Terrace Ledge Kink (TLK) model by Kossel and Stranski).

Mersmann (1995) suggests that a molecule arrives as a “package” at the binding location. In the case of struvite, that would mean a package of NH_4^+ , Mg^{2+} and PO_4^{3-} would form an aqueous struvite complex in the bulk solution which then diffuses through the boundary layer. In the case of heavy metal substitutions for magnesium or ammonium, the substitution would already take place during the complex formation in the bulk solution. Also possible is that ions, although already incorporated into the lattice, are replaced by other ions. This happens mostly to ions located on an edge of the crystal (Kruger and Vinx, 1974).

2.4 Practical parameters influencing the crystallisation process of struvite in urine

Struvite formation is influenced by many practical factors. In a laboratory setting, these factors are relatively easy to adapt; in a full scale application it may be more difficult to change them.

2.4.1 pH

One of the major influencing parameters is pH. The activities of both NH_4^+ and PO_4^{3-} are strongly pH dependent: with increasing pH values the activity of PO_4^{3-} increases while NH_4^+ becomes less prevalent. Because of the ammonia abundance in urine, the availability of phosphorus is more determining for struvite precipitation. For struvite, precipitation has been reported for pH values between 7 and 11 (Doyle and Parsons, 2002), with a minimum solubility at pH 9 (Münch and Barr, 2001; Nelson *et al.*, 2003). pH can also affect struvite morphology. Matynia *et al.* (2006) demonstrated that an increase of pH from 8 to 11 could significantly decrease the mean crystal size of struvite formed in synthetic solutions. Le Corre *et al.* (2006) showed a relationship between pH and the zeta-potential of struvite. Zeta-potential can interfere with agglomerate formation. Hence, a change in pH can lead to significant differences in crystal size.

2.4.2 Temperature

Although not as obvious as pH and supersaturation, temperature influences struvite solubility, both over the solubility constant and the reaction rate (Durrant *et al.*, 1999). Aage *et al.* (1997) and Burns and Finlayson (1982) showed the influence of the temperature on the solubility product of struvite. Temperature is also of influence on crystal growth (Jones, 2002; see section 2.3). Struvite solubility was shown to increase with temperature from $0.3 \cdot 10^{-14}$ at 10 °C to an optimum of $3.73 \cdot 10^{-14}$ at 50°C (Aage *et al.*, 1997). As the solubility product is linked to the supersaturation state of the solution in which crystals may occur, the precipitation of struvite is more difficult to obtain at high temperatures (Le Corre, 2006). An additional factor is that the region of ammonia evaporation must be avoided. Temperature is known to affect crystal growth as it affects the relative rates of diffusion and surface integration (Le Corre, 2006; Jones 2002). Both Babic-Ivancic *et al.* (2002) and Adnan *et al.* (2004) reported different temperatures to lead to different morphologies.

2.4.3 Precipitant addition rate

Addition of precipitant, which is magnesium in the case of struvite crystallisation from urine, can also influence the precipitation process in combination with stirring. If all precipitant is added at once, the degree of supersaturation upon addition is locally very high. This may lead to the production of many fines rather than fewer yet larger crystals (Adnan *et al.*, 2004).

2.4.4 Stirring

Turbulence is reported to contribute to struvite formation, with as main reason the local rise in pH caused by CO₂ stripping (Stratful *et al.*, 2004). Kim *et al.* (2009) mention that by accelerating the mixing in the process, the potential of struvite precipitation can be enlarged due to an enhancement of mass transport in the system.

Stirring can however also have negative effects. Wilsenach *et al.* (2007) found that stirring had virtually no effect on the soluble P effluent concentration, yet higher mixing speeds led to a higher percentage of scaling on the reactor wall. Additionally, high mixing speeds can accelerate nucleation rate and so limit crystal growth (Le Corre, 2006), and final crystal size may be reduced due to crystal breakage or shearing (Durrant *et al.*, 1999).

2.5 Magnesium

Magnesium is essential to all living cells. The adult human daily requirement of magnesium is about 0.3 g day^{-1} (Web elements). Hundreds of enzymes require magnesium in order to function (Magnesium For Life, 2009), and a magnesium deficit can lead to many types of health problems. For plants, magnesium is essential since it forms the metallic ion at the centre of chlorophyll. Therefore, magnesium is a common additive to fertilisers (Mengel *et al.*, 2001). Another common application in agriculture is as a supplement to fodder for livestock.

Magnesium is derived from ores and from salt containing water bodies. The most common magnesium ores are dolomite (magnesium and calcium carbonate, $\text{MgCO}_3 \cdot \text{CaCO}_3$) and magnesite (magnesium carbonate, MgCO_3) (USGS, 2009). Less common are brucite (magnesium hydroxide, Mg(OH)_2) and carnallite (a composite of magnesium potassium chlorides $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) (Magnesium Processing, 2009). Magnesium chloride is recovered from naturally occurring brines (Great Salt Lake, Dead Sea) and the less concentrated ocean water.

For the choice of an appropriate magnesium source as a struvite precipitant, several aspects play a role. The magnesium source has to be soluble in hydrolysed urine, i.e. under alkaline conditions. In order to minimise transportation costs, the product should have a reasonable magnesium content (Gantenbein and Khadka, 2008). Final important aspect is the price. Because magnesium forms a global source for many different applications, the price is prone to fluctuation. For magnesium chloride used for struvite experiments, Celen and Türker paid \$0.31 per kilo in 2001, whereas for a pilot project in Sneek, the Netherlands in early 2008, the project manager of Landustrie calculated with €525 per 1000 kilo (\$0.74 per kilo). Struvite precipitation can also be performed with lower grade magnesium sources such as bittern, a rest product from table salt production consisting of mainly magnesium chloride (Lee, 2003). The application of a rest product can reduce the cost strongly. However, when struvite is to be marketed, a constant reliable product has to be guaranteed, which may not always be possible when a product with unknown composition is applied.

2.6 References

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Struvite precipitation thermodynamics in source-separated urine

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Abstract

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$) precipitation eliminates phosphate efficiently from urine, a small but highly concentrated stream in the total flux of domestic wastewater. Precipitation experiments with hydrolysed urine evaluated the solubility product of struvite. The stored and fully hydrolysed urine had an ionic strength of between 0.33 and 0.56 M and required the estimation of activity coefficients. From our data, we identified the Davies approximation with the two constants $A=0.509$ and $B=0.3$ as agreeing best with our laboratory results. The standard solubility product $K_s^0 = f_1 \cdot [\text{NH}_4^+] \cdot f_2 \cdot [\text{Mg}^{2+}] \cdot f_3 \cdot [\text{PO}_4^{3-}]$ ($[]$ = concentration of the species, f_x = corresponding activity coefficient) of struvite in urine was found to be $10^{-13.26 \pm 0.057}$ at 25 °C and the enthalpy of struvite formation ΔH was $22.6(\pm 1.1) \text{ kJ mol}^{-1}$. The equilibrium calculations required the following dissolved complexes: $[\text{MgCO}_3]_{\text{aq}}$, $[\text{MgHCO}_3]^+$, $[\text{MgPO}_4]$, $[\text{NH}_4\text{HPO}_4]^-$, and $[\text{NaHPO}_4]^-$ and to a lesser extent $[\text{MgSO}_4]_{\text{aq}}$ and $[\text{NH}_4\text{SO}_4]^-$. Organic complexes do not seem to influence the solubility product substantially.

For practical purposes, a conditional solubility product $K_s^{\text{cond}} = [\text{Mg}_{\text{aq}}] \cdot [\text{NH}_4^+ + \text{NH}_3] \cdot [\text{P}_{\text{ortho}}] = 10^{-7.57} \text{ M}^3$ was derived to calculate struvite solubility in urine at 25 °C, pH = 9.0 and ionic strength $I = 0.4 \text{ M}$ directly from measured concentrations.

Keywords: Struvite, activity coefficients, moderate ionic strength, enthalpy, urine, wastewater treatment

3.1 Introduction

Separate collection of human urine eliminates nutrients from domestic wastewater and substantially decreases the nutrient load to the treatment plant. Urine contains most of the nutrients excreted by humans: 85–90% nitrogen, 50–80% phosphorus, and 80–90% potassium (Larsen and Gujer, 1996). Collecting this highly concentrated waste stream separately enables elimination as well as reuse of these nutrients (Lienert and Larsen, 2004, Maurer *et al.*, 2006). The formation of magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), also known as struvite, is attractive because it feeds two dominant wastewater nutrients into a good slow-release fertiliser (Bridger *et al.*, 1962, Johnston and Richards, 2003).

Many researchers have examined struvite precipitation in waste streams (Aage *et al.*, 1997, Battistoni *et al.*, 1997, Burns *et al.*, 2001, Doyle and Parsons, 2002, Jaffer *et al.*, 2002, Adnan *et al.*, 2004, Wu *et al.*, 2005). Their results indicate that stored urine offers optimal chemical conditions for struvite precipitation. Udert *et al.* (2003a) showed that struvite precipitation is triggered in urine collection systems by hydrolysis of urea and limited by the availability of magnesium.

Urine has a much higher ionic strength than wastewater. With typical values between 0.3 and 0.6 M, it resembles seawater but has strong variations in chemical composition and the presence of substances with complex-forming properties such as carbonate and phosphate. Precise calculation of the solubility product therefore requires correct calculation of the activity coefficients and consideration of other equilibrium reactions that might influence the activity of the ions responsible for struvite precipitation.

In investigating the thermodynamic aspects of struvite precipitation in source-separated urine, estimations of the solubility product and the enthalpy of struvite formation are derived from

experimental data. To do this, we need to examine the methods used to approximate the activity coefficient from the literature and to review the influence of possible equilibrium and complex-formation reactions. For practical purposes, a conditional solubility product is derived for urine that enables the fast estimation of the dissolved phosphate, magnesium and ammonium concentrations after struvite precipitation.

3.2 Background

3.2.1 Solubility Product

The standard solubility product is defined as

$$K_s^0 = f_1 \cdot [NH_4^+] \cdot f_2 \cdot [Mg^{2+}] \cdot f_3 \cdot [PO_4^{3-}] \quad (1)$$

where $[NH_4^+]$, $[Mg^{2+}]$ and $[PO_4^{3-}]$ are the concentrations and f_1 , f_2 and f_3 the activity coefficients (eq. 5) of the specific free ions of NH_4^+ , Mg^{2+} and PO_4^{3-} respectively.

When calculating the activities for the standard solubility product, speciation based on pH and all present ions has to be taken into account, as well as the determination of the activity factors. For a complex system like urine this is a tedious task. Since undiluted stored urine has a consistent composition in terms of ionic strength and pH, we can work with a conditional solubility product, which is defined here as a product of calculated total concentrations in a system in equilibrium:

$$K_s^{cond} = [NH_4^+ + NH_3] \cdot [Mg]_{aq} \cdot [P]_{ortho} \quad (2)$$

$[NH_4^+ + NH_3]$ represent the dissolved ammonia/ammonium, $[Mg]_{aq}$ the total dissolved magnesium and $[P]_{ortho}$ the total dissolved ortho-phosphate concentration. Because K_s^{cond} is determined for a specific matrix with fixed pH and ionic strength, it is valid for this matrix only (Stumm and Morgan, 1996). But, since K_s^{cond} is derived directly from calculated total concentrations, speciation or activity calculations become redundant in estimating maximum dissolved total concentrations.

Temperature corrections of the solubility product are performed with the Van't Hoff equation (Stumm and Morgan, 1996):

$$\frac{K_s(T_2)}{K_s(T_1)} = e^{\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (3)$$

in which $K_s(T_1)$ and $K_s(T_2)$ are the solubility products at temperatures T_1 and T_2 in Kelvin respectively, $R = 8.3145 \text{ J mol}^{-1}\text{K}^{-1}$ and ΔH is the formation enthalpy. All concentrations are given in $[M]$ or $[mM]$.

3.2.2 Activity coefficients

In undiluted and hydrolysed urine the concentrations are high enough to substantially influence the mobility and therefore the activity of single ions. Most relevant equilibrium constants, such as solubility constants, are consequently influenced by the ionic strength, and activity coefficients must be considered for all chemical calculations. As an example: in urine the struvite solubility product is

typically about 80 times higher (ionic strength = 0.4 M) than the calculations without activity coefficients would predict.

The ionic strength I is defined as (Stumm and Morgan, 1996):

$$I = 0.5 \cdot \sum_i (c_i \cdot z_i^2) \quad (4)$$

where: c_i is the concentration of ion i and z_i the charge of ion i . Typical values for the ionic strength of undiluted urine are between 0.3 and 0.6 M. This exceeds the valid range for most simple ion-pairing models for activity coefficients estimation, such as Debye-Hückel or Güntelberg approximations (Stumm and Morgan, 1996). Literature offers several methods of approximating activity coefficients for higher ionic strengths (see Maurer, 1983 and Bethke, 1996 for an extended overview), such as:

- Specific ion interaction models, such as the Harvie-Möller-Weare method (Harvie *et al.*, 1984), the Brønsted-Guggenheim-Scatchard approximation (Brønsted, 1922, Guggenheim, 1935, Scatchard, 1976) and the Pitzer method (Pitzer, 1979). The published parameter sets for these models are very accurate for seawater, but are not applicable to urine because of missing coefficients for important substances (ammonium, phosphate).
- The ion-specific method presented by Millero and Schreiber (1982) assigns individual activity coefficients to each substance. It uses the Pitzer coefficients to recalculate the existing thermodynamic equilibria for elevated ionic strengths. This approach is easy to implement in simulation software or spreadsheets.
- The Davies' approximation (Davies, 1962) applies the same activity coefficient to all ions with the same charge. It is a suitable approach for diluted urine with $I < 0.5$ M

$$-\log f_i = Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - BI \right) \quad (5)$$

where I is the ionic strength [M]; z_i is the charge of ion i ; $A = 0.509$ for water at 25°C, $B = 0.2$ or 0.3 as also suggested in the literature.

- The 'B-Dot' approach (Helgeson, 1969, Helgeson and Kirkham, 1974) is similar to Davies but applies a variable temperature-dependent \dot{B} instead of a constant B in eq.(5). The approach is widely applied in geochemical models such as the Geochemical Workbench (Bethke, 1994) or PHREEQC (Parkhurst and Appelo, 1999) and is reasonably accurate for ionic strengths up to 0.3-1M.

3.3 Material and Methods

3.3.1 Reagents, stock solutions and urine

For the equilibrium experiments, completely hydrolysed men's urine was collected from three waterless urinals and one NoMix toilet. Artificial urine was prepared as shown in Table 3-1.

Table 3-1: Composition of artificial urine solution in deionised water

Species	g L ⁻¹	M	Species	g L ⁻¹	ml L ⁻¹	M
Na ₂ SO ₄ water free	2.3	0.016	NaCl	3		0.051
KCl	3.4	0.046	NH ₄ HCO ₃	21		0.266
NH ₄ Cl	3.9	0.073	NH ₃ (25%)		17	0.228
NaH ₂ PO ₄	2.0	0.017				

(Udert, 2003c)

Magnesium was added in the form of a magnesium chloride solution (typically 1.7M). For acidification of the 20 ml samples 1.5 ml 2M hydrochloric acid was used. All chemicals used are analytical grade and originated from Merck (Switzerland).

3.3.2 Experimental set-up

Batch experiments were conducted in double-wall glass reactors (0.5-1 L). Mg:P ratios varied from 0.22:1 to 2:1. The reactors were stirred with a propeller stirrer at 300 rpm. The solution was kept at the desired temperature (5, 10, 20, 25 or 30°C). Initial pH was 9.0. Based on preliminary experiments an experimental time of 75 minutes was established. The pH was measured with a WTW 340i with Mettler Toledo gel probe and platinum reference electrode, and the data were logged. The reproducibility and stability of these measurements in high ionic strength solutions were confirmed. For analysis, 20 ml samples were taken and filtered through a Whatman GF/F glass fibre filter, and stored at 4 °C until analysis. The ammonia/ammonium was analysed photometrically with flow injection analysis (reaction with bromocresol purple, Foss FIA star 5000 Analyzer Gerber Instruments), phosphate with ion chromatography (Metrohm, column IonPac® AS12A, Dionex Corporation, Sunnyvale, Ca, USA) and magnesium with ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometer, Spectro Analytical Instruments, Kleve, Germany). Equilibrium calculations were performed with the PHREEQC programs (Version 2.10.0.0, Nov 2004, Parkhurst and Appelo, 1999) and the initial magnesium concentrations, the ΔH and the standard solubility product were estimated in AQUASIM (Reichert, 1994) with the same set of equilibrium reactions. All used thermodynamic data are referenced properly (Table 3-2).

Table 3-2: Thermodynamic equilibria for the source-separated urine system

Equilibrium					pK	Reference	
Mg ²⁺	+	H ₂ PO ₄ ⁻	↔	MgPO ₄ ⁻	+ 2H ⁺	12.96	Viellard and Tardy (1984)
Na ⁺	+	H ₂ PO ₄ ⁻	↔	NaHPO ₄ ⁻	+ H ⁺	6.01	
Mg ²⁺	+	H ₂ PO ₄ ⁻	↔	MgHPO ₄	+ H ⁺	4.3	
NH ₄ ⁺	+	HPO ₄ ²⁻	↔	NH ₄ HPO ₄ ⁻		-1.3	Martell <i>et al.</i> (1997)
Mg ²⁺	+	SO ₄ ²⁻	↔	MgSO ₄		-2.37	
NH ₄ ⁺	+	SO ₄ ²⁻	↔	NH ₄ SO ₄ ⁻		-1.03	
		H ₂ PO ₄ ⁻	↔	HPO ₄ ²⁻	+ H ⁺	7.21	Stumm and Morgan (1996)
		HPO ₄ ²⁻	↔	PO ₄ ³⁻	+ H ⁺	12.36	
Mg ²⁺	+	HCO ₃ ⁻	↔	MgHCO ₃ ⁺		-1.07	
Mg ²⁺	+	HCO ₃ ⁻	↔	MgCO ₃	+ H ⁺	7.35	
		HCO ₃ ⁻	↔	CO ₃ ²⁻	+ H ⁺	10.33	
		NH ₄ ⁺	↔	NH ₃	+ H ⁺	9.24	

All pK = - log (K) values are given for 25 °C and *I* = 0

3.4 Experiments, Results and Discussion

3.4.1 Experiments

In order to test the optimal reaction time, phosphate concentrations were followed over time during several precipitation experiments (Figure 3-1). It was observed that after 30 minutes minimal phosphate concentrations are reached at a detection limit of $0.30 (\pm 5\%) \text{ mgP L}^{-1}$ ($0.010 \pm 5\% \text{ mM}$). Re-measurements of samples from previous batch experiments confirmed our findings: after 24 months storage at 4°C the same dissolved magnesium, phosphate and ammonium concentrations were found (Table 3-3).

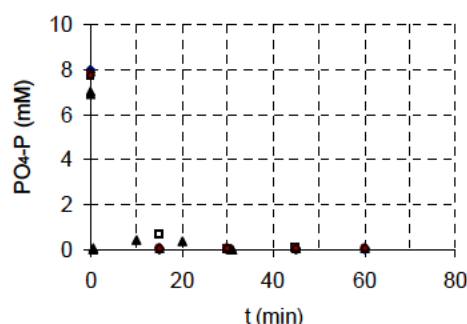


Figure 3-1. Phosphate concentration during several precipitation experiments over time. The phosphate concentrations during the standard batch experiments are stable well before 75 min.

Table 3-3: Re-measurement of 2 samples from previous batch precipitation experiments (identical to the experiments described in this paper: magnesium chloride added stored urine, pH 9.0)

Sample	t	Ion concentrations [mM]		
		PO ₄ -P	Mg	NH ₄ -N
A	0	7.74	12.4	386
	60 min	0.20	3.68	376
	24 months	0.19	3.64	376
B	0	7.74	12.4	386
	60 min	0.12	3.26	375
	24 months	0.12	3.45	371

After storage of the samples at 4°C for 24 months, the concentrations are the same as after 60 minutes of reaction time.

A set of 24 experiments was performed to identify the relevant equilibrium reaction in struvite precipitation, the standard solubility product, K_s^0 and its temperature dependency. Table 3-4 summarizes all the experiments performed.

Table 3-4: Initial values of batch experiments performed to determine the solubility product of struvite in fully hydrolysed source-separated urine (Experiment 1-5 and 9-24) and artificial urine (Exp. 6-8). The relative analysis precision (CV%) for ammonia/ammonium and phosphate is 5%, for magnesium 2%. The initial pH was 9.0. MgCl_2 was used as precipitant, except for experiment 13 (MgO) and 14 (Mg(OH)_2). Experiments 15-18 were carried out at different temperatures, all others at 25 °C.

Experiment identifier	T, °C	Ionic strength, M	$[\text{NH}_4^+ + \text{NH}_3]$, mM	$[\text{P}_{\text{ortho}}]$, mM	$[\text{Mg}]_{\text{aq}}$, mM	$\text{Mg}_{\text{initial}}:\text{P}_{\text{initial}}$, -
1	25	0.34	306	5.71	2.10	0.37
2	25	0.35	316	5.13	4.23	0.82
3	25	0.56	508	14.2	4.47	0.31
4	25	0.32	291	4.20	1.08	0.26
5	25	0.54	489	13.7	4.54	0.33
6	25	0.47	424	8.10	7.80	0.96
7	25	0.51	454	8.10	7.81	0.96
8	25	0.50	467	8.10	15.9	1.96
9	25	0.39	359	8.01	10.7	1.34
10	25	0.39	356	7.87	11.0	1.40
11	25	0.40	363	6.81	11.5	1.69
12	25	0.40	363	7.04	9.60	1.36
13	25	0.34	311	5.71	2.09	0.37
14	25	0.33	301	4.20	1.09	0.26
15	5	0.40	369	7.70	10.6	1.38
16	10	0.41	376	7.70	11.2	1.45
17	20	0.41	374	7.70	10.9	1.42
18	30	0.41	374	7.70	10.7	1.39
19	25	0.41	366	6.43	1.41	0.22
20	25	0.41	368	6.43	2.65	0.41
21	25	0.40	367	6.43	5.73	0.89
22	25	0.40	366	6.43	2.12	0.33
23	25	0.40	364	6.43	4.05	0.63
24	25	0.40	364	6.43	7.86	1.22

Experiments 6, 7 and 8 were conducted with artificial urine (Table 3-1), all others with men's urine from the collection system. The ionic strength is between 0.32 and 0.56 and the dissolved phosphate concentration between 4.2 and 14.2 mM. The following molar ratios of dissolved concentrations were determined (\pm standard deviation): $(\text{NH}_x):(\text{P}_{\text{ortho}}) = 54(\pm 8.4)$, $(\text{NH}_x):(\text{SO}_4^{2-}) = 38.7(\pm 2.1)$, $(\text{NH}_x):(\text{Cl}^-) = 2.8 (\pm 0.4)$, $(\text{NH}_x):(\text{Na}^+) = 3.7(\pm 0.1)$, $(\text{NH}_x):(\text{K}^+) = 7.6(\pm 0.8)$. The added magnesium to dissolved phosphate ratio was varied between 0.2 up to 2.0. Smaller ratios have the advantage that the dissolved phosphate concentration does not fall below the detection limit at the end of the experiment. The pH of the solution stayed 9.0 throughout the experiments and was not affected by the precipitation process due to the high buffer capacity of the ammonia / ammonium equilibrium and the high $(\text{NH}_x):(\text{P}_{\text{ortho}})$ ratio. The calcium concentrations were $0.7(\pm 0.1)$ mM.

3.5 Results

3.5.1 Standard solubility product, K_s^0 and temperature dependency

Table 3-5 shows the measured equilibrium concentrations and the calculated results. The calculations were performed with Davies' approximation for the activity coefficients and the equilibrium reactions in Table 3-2. The standard solubility product, K_s^0 , and the enthalpy, ΔH , were estimated as the best fit (least square method) of the dissolved magnesium and orthophosphate

concentrations, both simulated and measured. The graphical comparison in Figure 3-2 shows that the model agrees well with the measured data. In the Supplementary Information an XRD analysis of the product shows that the precipitate consists of 100% struvite (Figure SI-1). An overall standard solubility product for struvite was determined with $K_s^0 = 10^{-13.26}$ (25 °C, estimated standard deviation of $10^{0.057}$). Based on the experiments carried out at different temperatures (experiment numbers 15-18) a solubility temperature dependency ΔH of 22.6 kJ mol^{-1} (25 °C, estimated standard deviation of 1.1 kJ mol^{-1}) could be estimated.

If the formation of dissolved complexes is ignored but the acid-base equilibria and the influence of the ionic strength are included, a significantly higher solubility product is obtained ($K_s = 10^{-12.18}$, standard deviation: $10^{0.04}$).

Table 3-5: Measured and calculated equilibrium concentrations of the batch experiments.

Experiment identifier	[P _{ortho}] meas. mM	[Mg] _{aq} meas. mM	[P _{ortho}] calc. mM	[Mg] _{aq} calc. mM
1	3.65	0.04	3.64	0.02
2	0.97	0.05	0.98	0.07
3	9.78	0.02	9.78	0.01
4	3.13	0.01	3.14	0.02
5	9.17	0.02	9.16	0.01
6	0.41	0.11	0.47	0.17
7	0.43	0.11	0.47	0.17
8	0.01	7.69	0.01	7.69
9	0.02	2.73	0.03	2.74
10	0.02	3.18	0.03	3.19
11	0.06	4.77	0.02	4.74
12	0.06	2.61	0.03	2.59
13	3.65	0.04	3.64	0.02
14	3.13	0.01	3.14	0.02
15	0.03	2.96	0.01	2.96
16	0.04	3.52	0.01	3.51
17	0.05	3.29	0.02	3.26
18	0.07	3.09	0.03	3.06
19	5.06	0.05	5.04	0.02
20	3.83	0.07	3.81	0.03
21	0.87	0.18	0.81	0.11
22	4.35	0.06	4.33	0.02
23	2.44	0.08	2.42	0.04
24	1.04	1.56	0.06	1.49

Experiment 1-5 and 9-24 were carried out with fully hydrolysed source-separated urine, experiment 6-8 with artificial urine. MgCl_2 was used as precipitant, except for experiment 13 (MgO) and 14 (Mg(OH)_2). The standard solubility product K_s^0 was estimated as the best fit (least square method) to all experimental data.

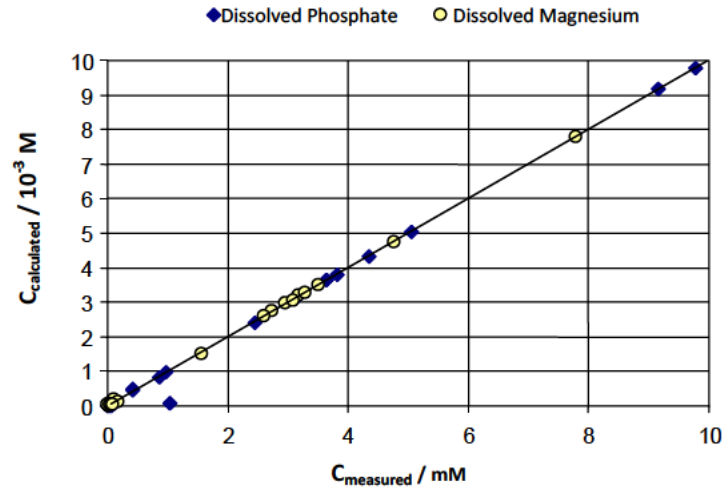


Figure 3-2. Comparison of measured and calculated concentrations of dissolved phosphate and magnesium in the experiments. The numbers are given in Table 3-5.

3.5.2 Evaluation of activity coefficient approximation

Three experiments (6, 7 and 8 in Table 3-4) were performed with a well-defined artificial urine solution (Table 3-1) to determine the most adequate approximation of the activity coefficients. Two experiments used an initial Mg:P ratio of 0.96 and one of 1.96. Quadruplicate samples were taken after three hours. Additional equilibrium calculations were performed with varying activity coefficient approximations: Davies (eq. 5) with $B=0.2$ and $B=0.3$, the B-dot method and the Millero - Schreiber method (1982).

Table 3-6: Comparison of four different activity coefficient approximation methods: B-Dot, Davies ($B=0.2$), Davies ($B=0.3$) and the Millero-Schreiber method.

Measured				Measured	Simulated			
Total concentrations (±standard dev.)				Conditional solubility, K_s^{cond}	Calculated conditional solubility, K_s^{cond}			
	$[\text{NH}_4^+ + \text{NH}_3]$ [M]	$[\text{P}]_{\text{ortho}}$ 10^{-4} [M]	$[\text{Mg}]_{\text{aq}}$ 10^{-4} [M]	10^{-8} [M ³]	B-Dot	Davies (B=0.2)	Davies (B=0.3)	Millero-Schreiber
						10^{-8} [M ³]		
6	0.416 (±0.0672)	4.15 (±0.125)	1.11 (±0.030)	1.92 (±0.257)	2.24	2.02	1.83	3.31
7	0.446 (±0.0252)	4.25 (±0.145)	1.06 (±0.030)	2.02 (±0.145)	2.41	2.16	1.95	3.47
8	0.459 (±0.0139)	0.052 (±0.026)	76.9 (±1.122)	1.82 (±0.913)	2.12	1.89	1.89	2.99

The conditional solubility product, K_s^{cond} (eq. 2) obtained from experiments with artificial urine ($\text{pH} = 9$) is compared with the four calculated results. The values in brackets are the standard deviations of the measurements.

Table 3-6 compares the measured conditional solubility product (eq. 2) with the four calculated results obtained from using the different activity coefficient approximations. The results indicate that Davies' approximation (eq. 5) with a B-factor of 0.3 fits the measured data best. All three solubility products do not deviate significantly from the measured value (Student t-test, 95% confidence interval). All equilibrium calculations are performed with the Davies approximation and the constants $A = 0.509$ and $B=0.3$ (eq. 5). Typical activity coefficients for an ionic strength of $I = 0.4$ M are: $f_1=0.73$, $f_2=0.29$, and $f_3 = 0.06$.

3.5.3 Equilibrium reactions

The equilibrium calculations revealed that the following dissolved complexes were formed at a level exceeding 3% relative to the total concentration of dissolved ammonium/ammonia, magnesium or phosphate: $[\text{MgCO}_3]_{\text{aq}}$, $[\text{MgHCO}_3]^+$, $[\text{MgPO}_4]^-$, $[\text{NH}_4\text{HPO}_4]^-$, and $[\text{NaHPO}_4]^-$. Their influence on the solubility product is therefore considered important and the corresponding equilibrium reactions (see Table 3-2) are included in the calculations. Due to the relatively low sulphate concentration (SO_4^{2-} : $14.8(\pm 0.8) \cdot 10^{-3}$ M) in the collected urine, $[\text{MgSO}_4]_{\text{aq}}$ and $[\text{NH}_4\text{SO}_4]^-$ are not foreseen to be formed in substantial amounts by the equilibrium model (less than 1% of magnesium and ammonium form complexes with sulphate).

3.6 Discussion

3.6.1 Standard solubility product, K_s^0

Many researchers report on the value of the standard solubility product of struvite, with $\text{p}K_s^0 = -\log(K_s^0)$ values ranging from 12.6 to 13.36 (Table 3-7). More values and good literature reviews on this topic are given in Buchanan *et al.* (1994) and Doyle and Parsons (2002).

Table 3-7: Standard solubility product $\text{p}K_s^0 = -\log(K_s^0)$ of struvite as reported in the literature

$\text{p}K_s^0$	T, °C	Speciation	Ionic strength, M	Reference
12.6	25	No	Negligible	Bube (1910)
13.15	25	Yes	0	Taylor <i>et al.</i> (1963)
13.12	25	Yes	0	Burns and Finlayson (1982)
12.97	35			
13.26	25	Yes	0	Ohlinger <i>et al.</i> (1998)
13.36	25	Yes	0	Babic-Ivancic <i>et al.</i> (2002)
13.27	37			
13.27	10	No	0	Aage <i>et al.</i> (1997)
12.93	25			
12.80	30			

A value of 12.6 was first reported by Bube in 1910. It was obtained at 25° C and negligible ionic strength and is commonly used in water chemistry texts today (Snoeyink and Jenkins, 1980, Stumm and Morgan, 1996), although no speciation was taken into account. In 1963, Taylor *et al.* reported a value of $13.15(\pm 0.1)$, calculated with an ionic strength obtained with the Güntelberg approximation. Burns and Finlayson (1982), Ohlinger *et al.* (1998) and Babic-Ivancic *et al.* (2002) determined $\text{p}K_s^0$ values of $13.12(\pm 0.05)$, $13.26(\pm 0.04)$ and $13.36(\pm 0.284)$ respectively. The standard solubility product of $\text{p}K_s^0 = 13.26(\pm 0.06)$ derived in this work agrees well with these literature results. All these approaches consider the ionic strength and additional equilibrium reactions (besides the acid-base reactions of the reactants).

3.6.2 Temperature dependency

The enthalpy determined from the data does not correspond to a real reaction enthalpy due to the missing temperature correction of the other equilibrium reactions. Nevertheless, the struvite solubility is shown to rise with increasing temperature ($\Delta H > 0$). This agrees well with the literature data (Burns and Finlayson, 1982, Aage *et al.*, 1997, Babic-Ivancic *et al.*, 2002, see also Table 3-7).

3.6.3 Equilibrium reactions

In the literature, the standard solubility products are determined exclusively in chemically well-defined matrices and at relatively low ionic strengths. The chemical speciation in these calculations therefore considers various magnesium-phosphate complexes and reactions between magnesium and ammonium (Doyle and Parson, 2002). The high amounts of sodium, ammonium, carbonate and sulphate are characteristic for urine. Our calculations showed that complex formation ($[\text{MgCO}_3]_{\text{aq}}$, $[\text{MgHCO}_3]^+$, $[\text{MgPO}_4]^-$, $[\text{NH}_4\text{HPO}_4]^-$, and $[\text{NaHPO}_4]^-$) has a substantial influence on the number of free ions that participate in struvite formation. Other complexes, notably with calcium and sodium, have no substantial influence. In the Supplementary Information a table is given with all complexes considered containing at least one struvite component (Table SI-1). Due to the relatively low sulphate (SO_4^{2-} : $14.8(\pm 0.8) \cdot 10^{-3}$ M) concentration in the collected urine, $[\text{MgSO}_4]_{\text{aq}}$ and $[\text{NH}_4\text{SO}_4]^-$ formation are not expected by the equilibrium model in substantial amounts (less than 1% of magnesium and ammonium form complexes with sulphate). However, this may change in cases where more sulphate is present.

It was reported that citrate and the calcium-binding protein calprotectin have a negative effect on struvite crystal formation (Asakura *et al.*, 1998). Citrate as well as oxalate however are not present anymore in stored urine (Udert *et al.*, 2003b). Calprotectin limits the number of struvite crystals formed. However, the presence of calcium reduces this effect visibly at 0.4mM Ca already, from 1.0mM Ca no effect can be seen. We did not measure calprotectin, but due to the presence of calcium (0.7 ± 0.1 mM) the effect cannot be substantial. The good agreement of the determined K_s^0 with the literature data indicates that organic complexes do not seem to influence the solubility product substantially and therefore do not play any quantitative role in struvite precipitation in urine.

The large difference between the estimated standard solubility product with ($\text{p}K_s^0 = 13.26$) and without considering complex formation ($\text{p}K_s = 12.18$) makes clear that substantial fractions of dissolved magnesium, ammonium and phosphate are not freely available for precipitation in urine. But it must be emphasised that there are no independent measurements to confirm either the presence or the concentration of these complexes. They originate from a deduction process designed to fit the measured solubility of struvite in urine into the general framework of the literature on chemical equilibria. The findings for the approximation of the activity coefficients and the set of complexation reactions are consequently not independent of each other. However, the good agreement with the other struvite precipitation literature indicates that the combination of the Davies' approximation and the suggested set of equilibrium/complexation reactions form a consistent approach to modelling the thermodynamic behaviour of struvite precipitation in hydrolysed urine.

3.6.4 Conditional solubility product

The conditional solubility product K_s^{cond} (eq. 2) for struvite precipitation in urine can be calculated as $10^{-7.57} \text{ M}^3$ ($\text{pH} = 9$, $I = 0.4$ M and $T = 25^\circ\text{C}$). This value can be used to estimate the solubility of struvite in urine directly without any further computation¹. K_s^{cond} varies with the ionic strength and pH (Figure 3-2). Due to the strong ammonia/ammonium buffer system in hydrolysed urine, the pH does

¹ In conditional solubility product computations even pH specific calculations are superfluous.

not usually deviate substantially from 9. However, the ionic strength can vary strongly depending on the collection system and the nature of the urine and therefore has a strong influence on K_s^{cond} as shown in Figure 3-3.

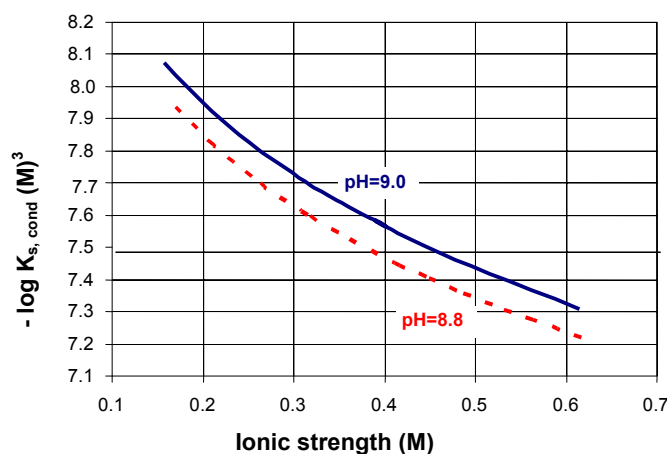


Figure 3-3: Computed conditional solubility product for the urine matrix. The initial magnesium concentration in the system was set equimolar to phosphate.

3.7 Conclusions

In this paper, we investigated the thermodynamic aspects of struvite precipitation in source-separated urine. The main conclusions are:

- For calculations with solutions comparable to urine with respect to ionic composition, the results of the Davies method ($A = 0.509$ and $B = 0.3$) agree best with the lab results.
- The most relevant equilibrium complexes are $[\text{MgCO}_3]_{\text{aq}}$, $[\text{MgHCO}_3]^+$, $[\text{MgPO}_4]^-$, $[\text{NH}_4\text{HPO}_4]^-$, and $[\text{NaHPO}_4]^-$ and to a lesser extent $[\text{MgSO}_4]_{\text{aq}}$ and $[\text{NH}_4\text{SO}_4]$.
- Together with a standard struvite solubility product K_s^0 was $10^{-13.26 \pm 0.06}$ a consistent method is presented to calculate the solubility of struvite in urine.
- The estimated formation enthalpy of struvite is $22.6 \pm 1.1 \text{ kJ mol}^{-1}$ which indicates that the struvite solubility rises with increasing temperatures.
- For specific use in urine ($\text{pH} = 9$, $I = 0.4 \text{ M}$, $T = 25^\circ\text{C}$), a conditional solubility product of $10^{-7.57} \text{ M}^3$ can be given. For other ionic strengths, K_s^{cond} can be taken from Figure 3-3.

3.8 Acknowledgements

The authors would kindly like to thank Jürgen Simons and Joachim Clemens from the University of Bonn, Department of Plant Nutrition for performing the XRD analysis of struvite.

3.9 References

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3.10 Supplementary Information

Table SI-1: Thermodynamic equilibria of all additional struvite components containing complexes considered in the model (cit=citrate, ox=oxalate), not yet mentioned in Table 2. All $pK = -\log(K)$ values are given for 25°C and $I = 0$.

Equilibrium				pK	Reference
Mg^{2+}	+	$H_2PO_4^-$	\leftrightarrow	$MgH_2PO_4^+$	Viellard and Tardy (1984)
Ca^{2+}	+	$H_2PO_4^-$	\leftrightarrow	$CaPO_4^- + 2H^+$	
Ca^{2+}	+	$H_2PO_4^-$	\leftrightarrow	$CaHPO_4^- + H^+$	
K^+	+	$H_2PO_4^-$	\leftrightarrow	$KHPO_4^- + H^+$	
NH_4^+	+	Cit^{3-}	\leftrightarrow	NH_4Cit^{2-}	Martell <i>et al.</i> (1997)
NH_4^+	+	Ox^{2-}	\leftrightarrow	NH_4Ox^-	
NH_4^+	+	$H_2PO_4^-$	\leftrightarrow	$NH_4H_2PO_4$	
Mg^{2+}	+	Cit^{3-}	\leftrightarrow	$MgCit^-$	Petitt and Powell (1997)
Mg^{2+}	+	Ox^{2-}	\leftrightarrow	$MgOx$	
Na^+	+	$H_2PO_4^-$	\leftrightarrow	$NaH_2PO_4^-$	
$2Na^+$	+	$H_2PO_4^-$	\leftrightarrow	$Na_2HPO_4^- + H^+$	
K^+	+	$H_2PO_4^-$	\leftrightarrow	$KH_2PO_4^-$	

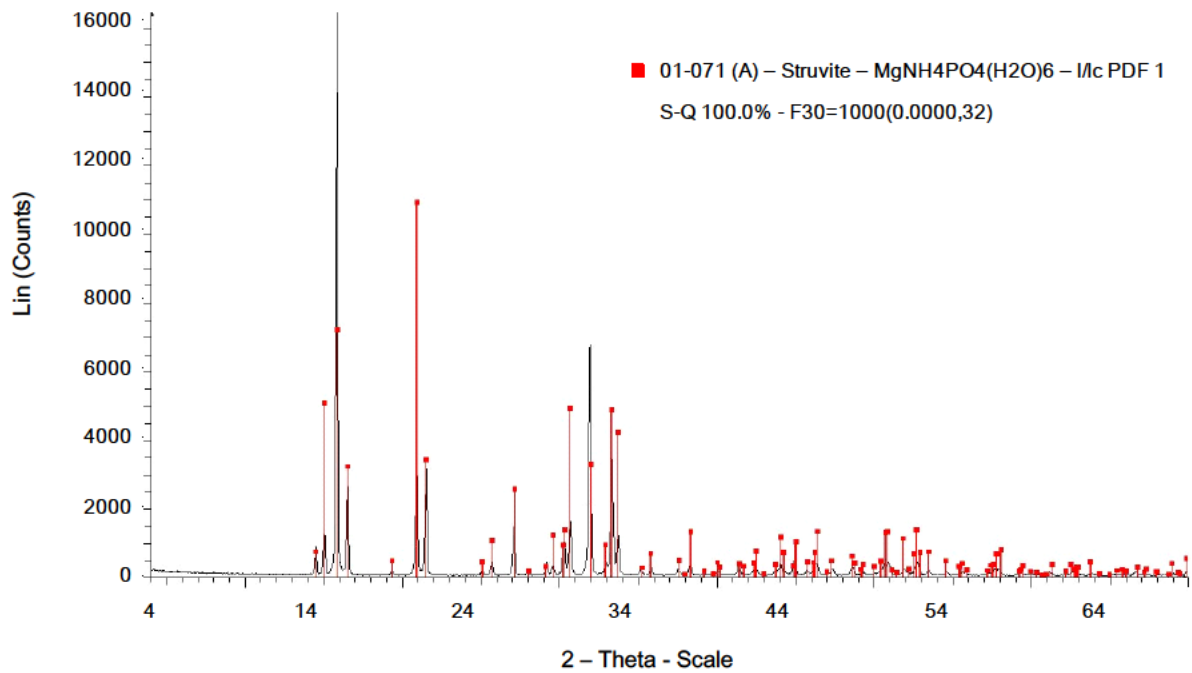


Figure SI-1: An X-ray Diffraction analysis of struvite produced from stored urine from the collection tank. Initial $PO_4\text{-P}$: x M, initial Mg added as $MgCl_2$: x M. Type: 2Th/Th locked – Start: 4.000° - End 70.000° - Step 0.020° - Step time: 1 s – Temperature: 25 °C (room temperature) – Time started: 2 s – 2-Theta: 4.000° - Theta: 2.000°.

**The behaviour of pharmaceuticals and heavy metals during struvite
precipitation in urine**

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Water Research 41 (9) 1859-1868

2007

Abstract

Separating urine from wastewater at the source reduces the costs of extensive wastewater treatment. Recovering the nutrients from urine and reusing them for agricultural purposes adds resource saving to the benefits. Phosphate can be recovered in the form of struvite (magnesium ammonium phosphate). In this paper, the behaviour of pharmaceuticals and heavy metals during the precipitation of struvite in urine is studied.

When precipitating struvite in urine spiked with hormones and non-ionic, acidic and basic pharmaceuticals, the hormones and pharmaceuticals remain in solution for more than 98%.

For heavy metals, initial experiments were performed to study metal solubility in urine. Solubility is shown to be affected by the chemical conditions of stored and therefore hydrolysed urine. Thermodynamic modelling reveals low or very low equilibrium solute concentrations for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) and lead (Pb). Experiments confirmed Cd, Cu and Pb carbonate and hydroxide precipitation upon metal addition in stored urine with a reaction half-life of ca. 7 days.

For all metals considered, the maximum specific metal concentrations per gram phosphate or nitrogen showed to be typically several orders of magnitudes lower in urine than in commercially available fertilisers and manure. Heavy metals in struvite precipitated from normal stored urine could not be detected.

Phosphate recovery from urine over struvite precipitation is shown to render a product free from most organic micropollutants and containing only a fraction of the already low amounts of heavy metals in urine.

Keywords: struvite, urine, nutrient recovery, pharmaceuticals, heavy metals

4.1 Introduction

Urine separation as a sustainable sanitary concept is gaining ground. Research on and implementation of this novel technology takes place in a growing number of countries (Peter-Fröhlich *et al.*, 2004, Wilsenach and van Loosdrecht, 2003, Kühni *et al.*, 2002, Larsen *et al.*, 2001, Johansson, 2001). The advantages of urine separation are considerable. Urine represents a small but concentrated stream, so by separating it from the main wastewater stream the nutrient load on the wastewater treatment plant can be reduced significantly (Larsen and Gujer, 1996). Additionally, the nutrients become available for recovery and re-use. Different techniques have been studied to remove and recover nutrients from urine, focusing mainly on nitrogen and phosphate (Maurer *et al.*, 2006, Udert *et al.*, 2003a, Pronk *et al.*, 2006a). An efficient phosphate removal technique is the precipitation of struvite. Struvite is a crystal built up from magnesium, ammonium and phosphate in a 1:1:1 molar ratio. Its precipitation from urine is a fast and undemanding process with respect to energy and necessary chemicals. Due to its low solubility in hydrolysed urine (pH 9) the addition of magnesium causes the solution to be supersaturated with struvite, leading to immediate precipitation (Rontelap *et al.*, 2007).

Struvite can be used as a fertiliser in agriculture (Bridger *et al.*, 1962, Johnston and Richards, 2003). Separate collection of urine, therefore, offers an opportunity to re-use nutrients directly as fertilisers. However, urine also contains substances which are not desirable in agriculture. In a screening assay of 212 pharmaceuticals an average of 64% of each compound was excreted via urine (Lienert *et al.*, 2006). From urine-based fertiliser products, these substances may diffuse into the

aquatic environment or accumulate in soils and have an adverse effect on human health and environment (Sanderson *et al.*, 2003, Halling-Sorensen *et al.*, 1998). Although currently no specific threshold values are available for micropollutants in fertilisers, the introduction of potential hazardous substances into the environment should be avoided (Pronk *et al.*, 2006b).

Another potential threat is posed by heavy metals. Under normal circumstances the human intake of heavy metals is low, which is reflected by low concentrations in urine (Ciba-Geigy, 1977). However, their accumulation in the soil is a serious concern for sustainable agriculture. Therefore, strict regulations are in place for heavy metal concentrations in fertiliser products.

In this paper we quantify the incorporation of pharmaceuticals, hormones and heavy metals to be incorporated into struvite during precipitation in source-separated human urine.

To study the behaviour of pharmaceuticals and hormones, experiments with spiked urine are carried out in a batch as well as a continuous flow set-up. The specific metal concentrations per gram of phosphorus and nitrogen are calculated and compared to the values for existing industrial fertilisers. To gain more insight into the behaviour of metals in urine, we perform a kinetic study and set up a thermodynamic model to predict equilibrium concentrations. By performing struvite precipitation experiments in heavy metal-spiked urine we investigate the possibility of metal contamination in struvite. No risk or hazard assessments are performed, rather data are provided which can be used in other studies which aim to perform a comprehensive risk analysis.

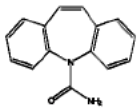
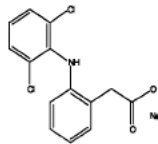
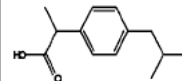
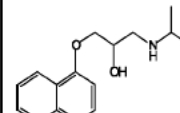
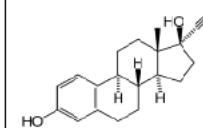
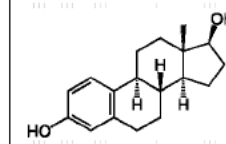
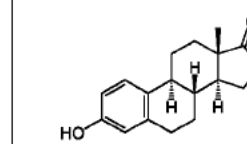
4.2 Background

4.2.1 Pharmaceuticals and hormones

Pharmaceuticals, hormones and their metabolites found in urine form a broad group of anthropogenic organic chemicals with a variety of structures. Some molecules contain ionic groups (e.g. carboxyl groups) and are, therefore, strongly influenced by pH (Schwarzenbach *et al.*, 2003). Both ionic and non-ionic organic molecules are reported to adsorb to the surface of inorganic minerals (Clausen *et al.*, 2001).

For this study, a mixture of commonly applied pharmaceuticals and hormones is used. Non-ionic (ethinylestradiol, carbamazepine) as well as acidic (diclofenac, ibuprofen) and basic (propranolol) compounds are represented. At the pH of urine (pH 9) propranolol is partially cationic, whereas ibuprofen and diclofenac are completely anionic. The characteristics of the micropollutants involved are shown in Table 4-1.

Table 4-1: Characteristics of pharmaceuticals and synthetic hormones spiked to urine (dissociation constants estradiol and estrone: Lewis and Archer, 1979; other source references see Pronk *et al.*, 2006b).

	Carbamazepine	Diclofenac	Ibuprofen	Propranolol	Ethinylestradiol (EE2)	Estradiol (E2)	Estrone (E1)
Function	Anti-epileptic	Non-steroidal anti-inflammatory	Non-steroidal anti-inflammatory	Anti-hypertention, betablocker	Synthetic steroid oral contraceptive	Natural hormone	Natural hormone
CAS nr.	298-46-4	15307-86-5	15687-27-1	525-66-6	57-63-6	50-28-2	53-16-7
Dissociation constant	- <i>neutral</i>	pK _a 3.99 <i>acidic</i>	pK _a 4.45 <i>acidic</i>	pK _a 9.24 <i>basic</i>	- <i>neutral</i>	pK _a 10.71 <i>basic</i>	pK _a 10.77 <i>basic</i>
Molecular weight (D)	236.27	182.68	206.29	259.35	296.39	272.4	270.4
Log K _{ow}	2.45	4.51	3.97	3.48	4.2	3.9	3.4
Structure							

4.2.2 Heavy metals

Heavy metals enter the human body mainly through nutrition. Additionally, uptake can occur through the skin and via the lungs. Depending on the type of metal, metal speciation and physical condition, the metals are either adsorbed and accumulated, or blocked by the intestinal tract and excreted (Nriagu, 1984). This might cause elevated levels of heavy metal in the collected urine. Moreover, corrosion of piping material (e.g. lead or copper) used to transport drinking water and to collect urine forms an important source of contamination.

Heavy metals can be incorporated into the crystal lattice or sorbed to the surface of struvite. Arsenate (AsO_4^{3-}) can substitute for phosphate. Substitution for both the magnesium and the ammonium ion within the struvite molecule is reported in literature. Ammonium was reported to be partly substituted by potassium, rubidium, caesium and tellurium (Banks *et al.*, 1975, Mathew and Schroeder, 1979). Magnesium was reported to be replaceable by cadmium (Ravikumar *et al.*, 2002), zinc (Chand and Agarwal, 1991) and nickel (Abbona *et al.*, 1994). Trace impurities in natural struvites, such as traces of sodium, manganese, iron and calcium were also reported (Chand and Agarwal, 1991). No thermodynamic data was reported for the formation of these struvite analogues.

4.3 Material and methods

4.3.1 Filters, reagents, stock solutions and urine

Whatman GF/F filters originated from American Membrane Corporation, Michigan, 0.45 μm membrane filters from Hach Lange GmbH, Düsseldorf. All pharmaceuticals were obtained from Sigma (Buchs, Switzerland), all other chemicals from Merck (analytical quality). A concentrated stock solution with pharmaceuticals was produced containing $2.24 \cdot 10^{-2} \text{M}$ (4.10 gL^{-1}) diclofenac, $1.34 \cdot 10^{-2} \text{M}$ (2.76 gL^{-1}) ibuprofen, $5 \cdot 10^{-3} \text{M}$ (1.48 gL^{-1}) propranolol, $2 \cdot 10^{-2} \text{M}$ (4.73 gL^{-1}) carbamazepine, $7.4 \cdot 10^{-7} \text{M}$ ($200 \mu\text{gL}^{-1}$) estradiol E2 and $6.8 \cdot 10^{-7} \text{M}$ ($200 \mu\text{gL}^{-1}$) ethinylestradiol EE2. The saturated struvite solution consisted of 1.31g Na_2HPO_4 , 1.6g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.86ml NH_3 -25% dissolved in 1 L of deionised water. Arsenic standard (1000 mgL^{-1}) was obtained from Mallinckrodt Baker BV, Deventer, The Netherlands. For Cd, Co, Cr, Cu, Ni, and Pb Merck ICP standard solution VI (1000 mgL^{-1}) was used.

All experiments were carried out with slightly diluted men's urine collected from the storage tank connected to a urine collecting system at the Eawag institute (consisting of 3 waterless urinals and one NoMix toilet). The urine was completely hydrolysed and had a pH value of 9. The entire collection system (piping and tanks) is made of PE and PVC with rubber gaskets and all the urinals/toilets are either plastic or ceramic.

4.3.2 Experiments pharmaceuticals

Two initial batch experiments were carried out using a mixture of propranolol (3.0 mg L^{-1}), estrone (E1), estradiol (E2) and ethinylestradiol (EE2) (all $4 \mu\text{gL}^{-1}$). For the other experiments a pharmaceutical stock solution was used. Details of the pharmaceuticals are given in Table 4-1.

Duplicate batch experiments were carried out in 500ml glass cylinders. Four hundred millilitre urine was spiked with the pharmaceutical stock solution (initial concentrations are given in

Table 4-2). After addition of 120 mg magnesium (0.005 mol MgCl_2) the batches were stirred for 3 h to reach equilibrium.

A dynamic experiment was performed in a 1100ml glass continuous flow completely stirred tank reactor (CSTR). Influent and magnesium solution were added at a rate of 88 and 13 ml/h, respectively. Direct addition of the cocktail to the CSTR prevented biodegradation in the influent tank. Micropollutants were added with a glass syringe pump. After 12 h (approx. 1 HRT) micropollutant addition rate was adjusted from 1.2 ml h^{-1} to 0.6 ml h^{-1} . After a running time of 36 h, 2 samples were taken from the reactor and 3 from the well mixed effluent of the entire 36 h experiment.

All samples were divided into two fractions (weighed and measured in glass cylinders), and filtered using separate GF/F filters. Per sample, one filter was washed with 100 ml saturated struvite solution. Residues were re-dissolved in 250 ml 1.5 M hydrochloric acid and analysed for phosphate, magnesium, ammonium and relevant hormones and pharmaceuticals.

4.3.3 Experiments heavy metals

4.3.3.1 Batch experiment

Five hundred millilitre urine was spiked with $100 \mu\text{g L}^{-1}$ As, Cd, Co, Cu, Cr, Ni, and Pb. After 2 h equilibrating $6.2 \cdot 10^{-3} \text{ mol MgCl}_2$ (150mg Mg) was added as a concentrated solution. After being stirred for 3 h the solution was divided into four fractions and filtrated over GF/F filters. The filters were re-dissolved in 200ml 1.5M HNO_3 . Samples for phosphate, ammonium, magnesium and metal analysis were taken, from the solution before and after metal addition, from the four filtrates and from the acidic solutions containing the re-dissolved material from the filters.

4.3.3.2 Two weeks' metal precipitation:

Two hundred millilitre hydrolysed urine was spiked with, respectively 0, 200 and $500 \mu\text{g L}^{-1}$ As, Cd, Co, Cu, Cr, Ni, and Pb. The mixtures were shaken for 15 days in a lab shaker. Samples taken after 1, 7 and 15 days were filtrated using a GF/F filter, and subsequently using a $0.45 \mu\text{m}$ filter. The total experiment was carried out three times.

All metal samples and standards were digested by adding 2ml concentrated suprapure HNO_3 and 1ml H_2O_2 to 10 ml sample in pressure-resistant Teflon tubes, filled up to 25ml with de-ionised water and treated in an MLS 1200 Mega microwave (Egrolt AG, Switzerland). Only plastic ware, thoroughly cleaned with 1.5M HNO_3 , was used.

4.3.4 Analytical methods

Phosphate was analysed with ion chromatography (Metrohm, column IonPac® AS12A, Dionex Corporation, Sunnyvale, Ca, USA). Heavy metal concentrations were measured with ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometer, Spectro Analytical Instruments, Kleve, Germany).

E1, E2 and EE2 were measured with LC/MS/MS. Before analysis, the samples were brought to pH 5, spiked with a deuterated internal standard and concentrated with solid phase extraction (SPE) as described in Vermeirssen (2005). Pharmaceuticals were measured with HPLC (fluorescence detection for propranolol and ibuprofen, UV detection for diclofenac and carbamazepine) as

described in Pronk *et al.* (2006b). Standard deviations were 2% for propranolol, ibuprofen and diclofenac, 3% for carbamazepine.

4.4 Results and discussion

4.4.1 Pharmaceuticals

Initial batch experiments were carried out with struvite precipitation in urine spiked with propranolol and the hormones estrone (E1), estradiol (E2) and ethinylestradiol (EE2). The experiments revealed that of the recovered fractions (mass sum of filtrate and re-dissolved struvite), 99%, 97%, 95% and 100% of respectively propranolol, E1, E2 and EE2 remained in solution.

Similar results were obtained in batch and continuous experiments with urine spiked with a broader spectrum of pharmaceuticals. In Table 4-2 the ion and pharmaceutical concentrations of these experiments are given. After struvite precipitation, $94.7 \pm 1.2\%$ (\pm standard deviation) propranolol, $99.6 \pm 0.6\%$ ibuprofen, $99.9 \pm 0.6\%$ diclofenac and $96.4 \pm 1.5\%$ carbamazepine of the recovered pharmaceuticals remained in solution. Washing off attached water by rinsing the crystals resulted in a lower amount of pharmaceuticals in the re-dissolved fraction: $1.8 \pm 0.8\%$ for propranolol, $0.1 \pm 0.2\%$ for carbamazepine and 0.0% for ibuprofen and diclofenac (Table 4-2). A cleaner struvite product can thus be obtained when the crystals are rinsed after filtration. The mass of pharmaceuticals can be related to the given nitrogen and phosphorus content to determine specific pharmaceutical concentrations.

No difference can be observed between recovery ratios in batch and continuous experiments. The concentration in the reactor and effluent are calculated on the basis of the stock solution.

A mass balance was made for all fractions in two batch experiments is shown in Table 4-3. It was shown that > 95% of all masses were recovered, except for carbamazepine in batch 1. This lower recovery for carbamazepine was not observed in other experiments and might have been caused by contamination.

In conclusion it can be said that only small amounts of pharmaceuticals attach to struvite crystals when precipitating struvite in human urine, in both batch and CSTR precipitation processes. Washing the struvite after filtration removes attached urine solution and produces even cleaner crystals.

Table 4-2: Concentrations in batch and CSTR experiments, measured with IC (phosphate), ICP-OES (magnesium) and HPLC (pharmaceuticals).

			PO ₄ -P [mg.L ⁻¹]	Mg [mg.L ⁻¹]	Propranolol [mg.L ⁻¹]	Ibuprofen [mg.L ⁻¹]	Diclofenac [mg.L ⁻¹]	Carbamazepine [mg.L ⁻¹]
Detection limits (LOD)			1	1	0.04	0.04	0.06	0.06
Experiment identifier								
1	Batch	Initial	255	-	19.65	37.84	54.12	63.90
		Filtrate	2	56	19.09	37.88	52.88	53.35
		Dissolved struvite	278	241	0.15	<LOD	<LOD	0.20
2	Batch	Initial	255	-	19.86	36.95	54.15	53.99
		Filtrate	2	76	19.53	37.74	53.35	54.75
		Dissolved struvite	286	214	0.15	<LOD	<LOD	0.14
3	CSTR	Reactor, calculated		-	9.10	16.71	24.80	28.69
		Filtrate	3	18	7.89	20.73	24.44	24.47
		Dissolved struvite	302	242	0.15	<LOD	<LOD	<LOD
4	CSTR	Reactor, calculated		-	9.10	16.71	24.80	28.69
		Filtrate	3	20	8.47	20.79	24.24	25.48
		Dissolved struvite	337	272	0.14	<LOD	<LOD	<LOD
5	CSTR	Mixed effluent, calculated		-	8.68	16.15	23.96	27.67
		Filtrate	31	<LOD	8.71	19.71	24.14	24.92
		Dissolved struvite	214	173	0.27	<LOD	<LOD	0.65
6	CSTR	Mixed effluent, calculated		-	8.68	16.15	23.96	27.67
		Filtrate	24	<LOD	10.26	22.69	27.49	28.04
		Dissolved struvite	211	169	0.24	<LOD	<LOD	<LOD
7	CSTR	Mixed effluent, calculated		-	8.68	16.15	23.96	27.67
		Filtrate	25	<LOD	9.02	19.75	25.07	25.19
		Dissolved struvite	219	174	0.20	<LOD	<LOD	<LOD

In all experiments the pH was 9, temperature 25°C. The concentrations in the redissolved rinsed residues are calculated back to the original solution.

Since the CSTR has not been operated in a steady state, the concentration in the reactor and the total concentrations in the effluent had to be obtained from a dynamic analysis according to $C_{tot} = (C_{\infty} - C_0) \cdot (1 - \exp(-t/\Theta))$, where t is the time since the change of operation, Θ the hydraulic retention time, C_0 is the concentration before change of operation and C_{∞} is the new steady-state concentration.

<LOD: Below limit of detection

Table 4-3: Masses of phosphate, magnesium and spiked pharmaceuticals for the total initial solutions, the filtrate and the re-dissolved struvite, in two batch experiments.

			PO ₄ -P [mg]	Mg [mg]	Propranolol [mg]	Ibuprofen [mg]	Diclofenac [mg]	Carbamazepine [mg]
Experiment identifier								
1	Batch	Total	103.7 100%	120.0 100%	8.00 100%	15.40 100%	22.03 100%	26.00 100%
		Filtrate	0.75 0.7%	22.9 19.1%	7.62 95.3%	15.28 99.2%	21.39 97.1%	21.59 83.0%
		Struvite	107 103.2%	93.7 78.0%	0.20 2.4%	0.10 0.7%	0.02 0.01%	0.28 1.1%
		Recovery	103.9%	97.1%	97.8%	99.9%	97.2%	84.1%
2	Batch	Total	103.5 100%	120.0 100%	8.07 100%	15.01 100%	22.00 100%	21.94 100%
		Filtrate	0.77 0.7%	27.35 22.8%	7.79 96.6%	14.82 98.7%	21.56 98.0%	21.88 99.8%
		Struvite	106.9 103.1%	87.31 72.75%	0.21 2.6%	0.09 0.6%	0.02 0.1%	0.27 1.2%
		Recovery	103.8%	95.6%	99.1%	99.3%	98.1%	101.1%

4.4.2 Heavy metals

4.4.2.1 Precipitation potential of heavy metals

The metal precipitation potential in urine was studied using a thermodynamic chemical equilibrium model developed with PHREEQC (Parkhurst and Appelo, 1999). Calculations were performed using the Davies activity coefficient approximation. The standard database PHREEQC.dat was extended with all relevant chemical equilibrium constants for metal complexes from Stumm and Morgan (1996) and Viellard and Tardy (1984) (Table 4-4). As arsenic is present as HAsO_4^{2-} and H_2AsO_4^- at pH 9 it reacts similarly to phosphoric acid and will not precipitate with carbonates and hydroxides.

Table 4-4: Complexation reactions added to the standard database PHREEQC.dat.

Equilibrium	logK	Equilibrium	logK
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	0.5	$\text{Ni}^{2+} + \text{OH}^- = \text{NiOH}^+$	4.1
$\text{Co}^{2+} + \text{OH}^- = \text{CoOH}^+$	4.3	$\text{Ni}^{2+} + 2\text{OH}^- = \text{Ni(OH)}_2$	9
$\text{Co}^{2+} + 2\text{OH}^- = \text{Co(OH)}_2$	9.2	$\text{Ni}^{2+} + 3\text{OH}^- = \text{Ni(OH)}_3^-$	12
$\text{Co}^{2+} + 3\text{OH}^- = \text{Co(OH)}_3^-$	10.5	$\text{Ni}^{2+} + \text{SO}_4^{2-} = \text{NiSO}_4$	2.3
$\text{Co}^{2+} + \text{SO}_4^{2-} = \text{CoSO}_4$	2.4	$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+$	0.6
$\text{Co}^{2+} + \text{H}^+ + \text{PO}_4^{3-} = \text{CoHPO}_4$	15.5	$\text{Ni}^{2+} + \text{H}^+ + \text{PO}_4^{3-} = \text{NiHPO}_4$	15.4
$\text{Co}^{2+} + \text{H}_2\text{PO}_4^- = \text{CoHPO}_4(\text{s}) + \text{H}^+$	0.49	$\text{Ni}^{2+} + 2\text{OH}^- = \text{Ni(OH)}_2(\text{s})$	17.2
$\text{Co}^{2+} + 2\text{OH}^- = \text{Co(OH)}_2(\text{s})$	15.7	$\text{Ni}^{2+} + \text{Ni}_3^{2-} = \text{NiCO}_3(\text{s})$	6.9
$\text{Co}^{2+} + \text{CO}_3^{2-} = \text{CoCO}_3(\text{s})$	10	$\text{Cr}^{3+} + \text{OH}^- = \text{CrOH}^{2+}$	10
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} = \text{Cu(CO}_3)_2^{2-}$	10.2	$\text{Cr}^{3+} + 2\text{OH}^- = \text{Cr(OH)}_2^+$	18.3
$\text{Cu}^{2+} + \text{HPO}_4^{2-} = \text{CuHPO}_4$	16.5	$\text{Cr}^{3+} + 3\text{OH}^- = \text{Cr(OH)}_3$	24
$\text{Cu}^{2+} + \text{H}_2\text{PO}_4^- = \text{CuH}_2\text{PO}_4^+$	21.4	$\text{Cr}^{3+} + 4\text{OH}^- = \text{Cr(OH)}_4^-$	28.6
$3\text{Cu}^{2+} + 2\text{H}_2\text{PO}_4^- = \text{Cu}_3(\text{PO}_4)_2(\text{s}) + 4\text{H}^+$	2.21	$3\text{Cr}^{3+} + 4\text{OH}^- = \text{Cr}_3(\text{OH})_4^{5+}$	47.8
$\text{Cu}^{2+} + \text{CO}_3^{2-} = \text{CuCO}_3(\text{s})$	9.6	$\text{Cr}^{3+} + \text{HPO}_4^{2-} = \text{CrHPO}_4^+$	2.2 ¹
$\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu(OH)}_2(\text{s})$	19.3	$\text{Cr}^{3+} + \text{H}_2\text{PO}_4^- = \text{CrH}_2\text{PO}_4^{2+}$	2.6 ¹
$3\text{Pb}^{2+} + 2\text{PO}_4^{3-} = \text{Pb}_3(\text{PO}_4)_2(\text{s})$	43.5	$\text{Cr}^{3+} + 3\text{OH}^- = \text{Cr(OH)}_3(\text{s})$	30
$\text{Pb}^{2+} + \text{H}^+ + \text{PO}_4^{3-} = \text{PbHPO}_4(\text{s})$	23.8		

Data taken from Stumm and Morgan (1996) or 1 Viellard and Tardy (1984).

In this model the addition of 500 µg metals to 1 L unhydrolysed and 1 L hydrolysed urine was simulated. The main modelled complexes and precipitants, contributing more than 3% of the total mass of either dissolved or precipitated metals, are given in Table 4-5.

Under unhydrolysed conditions, i.e. pH 6 and no bicarbonate, only part of the copper and lead precipitate as metal phosphates, all other metals remain in solution. In hydrolysed urine however, with a pH of 9 and 170mM total carbonate, all metals (except arsenic) could potentially precipitate as metal carbonates and hydroxides to reach equilibrium.

Table 4-5: Modeled equilibria concentrations and the relevant complexes / precipitants (>3% of the total dissolved and precipitated mass, respectively), after addition of 500 µg metals to 1L unhydrolysed urine and hydrolysed urine.

Unhydrolysed urine				Hydrolysed urine			
	Dissolved at equilibrium	Main Dissolved	Precipitates	Dissolved at equilibrium	Main Dissolved	Precipitates	
	µg.L ⁻¹	Part of total		µg.L ⁻¹	Part of total		
Cd	500	100%	CdCl ⁺ Cd ²⁺ CdCl ₂ CdSO ₄	0.2	0.0%	Cd(CO ₃) ₂ ²⁻	CdCO ₃ (s)
Co	500	100%	Co ²⁺	3.06	0.6%	Co ²⁺ CoHPO ₄	CoCO ₃ (s)
Cr	500	100%	Cr(OH) ₂ ⁺ CrOH ²⁺	87.3	17.3%	Cr(OH) ₃ Cr(OH) ₄ ⁻ Cr(OH) ₂ ⁺	Cr(OH) ₃ (s)
Cu	4.4	0.9%	Cu ²⁺ CuCl ⁺ Cu ₃ (PO ₄) ₂ (s)	0.0	0.0%	CuCO ₃ (aq)	CuCO ₃ (s)
Ni	500	100%	Ni ²⁺ NiSO ₄ NiCl ⁺	19.6	3.9%	Ni ²⁺ NiHPO ₄ NiCl ⁺ NiOH ⁺	Ni(OH) ₂ (s)
Pb(II)	6.4	1.3%	PbCl ⁺ Pb ²⁺ PbHPO ₄ (s) PbSO ₄ PbCl ₂	0.2	0.0%	PbCl ⁺ Pb(OH) ₂ Pb ²⁺ PbOH ⁺	PbCO ₃ (s)

Initial values for unhydrolysed urine: pH 6.2, 0.48 gNH_x-N.L⁻¹, 9.25 g urea.L⁻¹, 0.74 gP_{tot}.L⁻¹, 0 g (HCO₃⁻+CO₃²⁻), hydrolysed urine pH 9.0, 4.79 gNH_x-N.L⁻¹, 0g urea.L⁻¹, 0.25 gP_{tot}.L⁻¹.

These thermodynamic considerations show that the processes during urine collection and storage can have a substantial impact on heavy metal solubility. The results indicate that the majority of the heavy metals, present in dissolved form in fresh urine, might precipitate during storage of urine. The same process was already shown for phosphate by Udert *et al.* (2003b): due to the pH increase caused by urea hydrolysis, phosphate precipitates with all available magnesium and calcium ions, resulting in a considerable decrease of the soluble phosphate concentration. In this calculation, we adopted the phosphate concentration for unhydrolysed undiluted urine from literature (0.74 g.L⁻¹, Udert *et al.*, 2003b) and our own measured phosphate concentration for hydrolysed urine (0.25 g.L⁻¹). The phosphate precipitated upon hydrolysis remains in the urine sludge found on the bottom of the urine collection tank, which is also where the metal precipitates would congregate. Although the metals are likely to precipitate as carbonates and not as phosphates (Table 4-5), it will be difficult to separate the precipitates, which may aggravate re-use of the phosphate in case of elevated metal concentrations. For optimal phosphate recovery it is therefore important to minimize the amount of (magnesium and calcium containing) flush water in order to minimize the amount of preliminary phosphate precipitation.

4.4.2.2 Metal precipitation in hydrolysed urine

In order to verify our modelled results we spiked hydrolysed urine with heavy metals and traced the dissolved concentrations over 2 weeks. The added metal concentrations were 0, 200 and 500 µg.L⁻¹ arsenic (As), cadmium (Cd), copper (Cu), cobalt (Co), chromium (Cr), nickel (Ni) and lead (Pb) (Figure 4-1). Over the course of the experiment Cd, Cu and Pb showed a clear precipitation process. Although the limited data do not permit the determination of a precise reaction rate and order, the results point out that the precipitation of Cd, Cu and Pb is a relatively slow reaction with a half-life of about 7 days. This indicates that a normal storage period from several weeks to several months is sufficient for precipitation of any elevated levels of cadmium, copper and lead. The metals will most likely be contained in the 'urine sludge' that forms during storage (Udert *et al.*, 2003b). For arsenic, cobalt, chromium and nickel no precipitation behaviour could be detected. These metals are known to be less reactive than Cd, Cu and Pb (Margerum *et al.*, 1978) and their precipitation may be kinetically hindered.

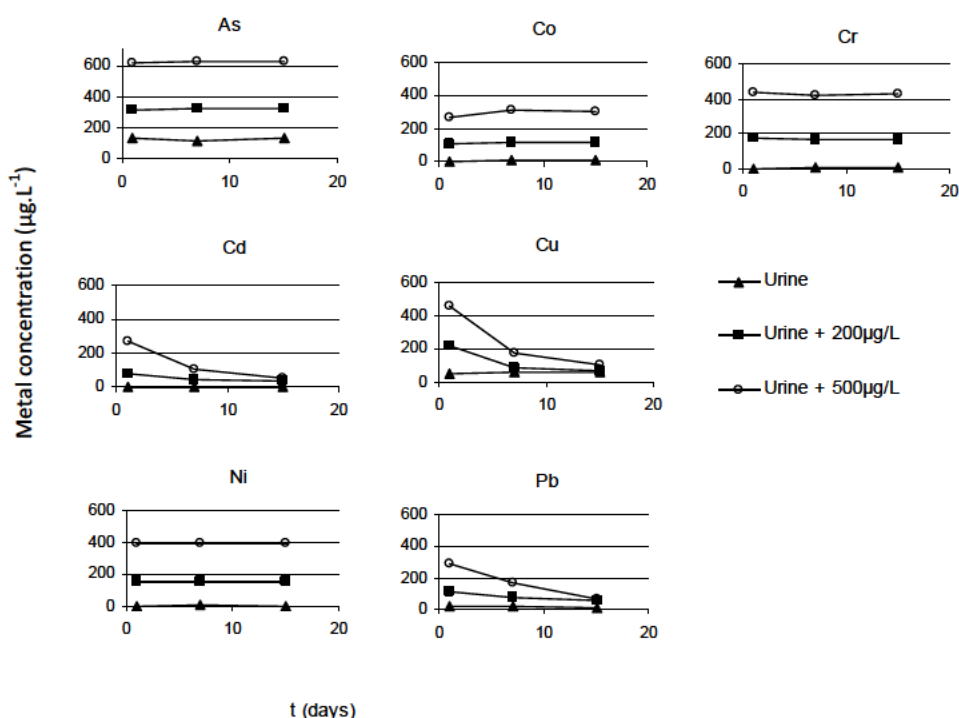


Figure 4-1: Soluble metal concentrations in hydrolysed urine spiked with metals at respectively 0, 200 and 500 $\mu\text{g.L}^{-1}$ over 15 days. Cd, Cu and Pb show a clear precipitation process over this period, As, Co Cr and Ni do not precipitate within two weeks. The averaged standard deviation for all measurements was 7.3% ($10.7 \mu\text{g.L}^{-1}$) for spiked and 25.5% ($5.1 \mu\text{g.L}^{-1}$) for non-spiked urine.

4.4.2.3 Distribution of heavy metals during struvite precipitation

In order to quantify possible incorporation of heavy metals in struvite precipitated from urine, batch experiments were carried out in urine spiked with heavy metal ($+100 \mu\text{g.L}^{-1}$). Table 4-6 shows the initial concentrations in the urine and the concentrations in the filtered and unfiltered fractions. The recovery range varied from 79% for Cd to 125% for Pb. The metals precipitated partly, ranging from 20% for As to 63% for Pb.

Table 4-6: Measured ion and dissolved metal concentrations in urine, before and after spiking $100 \mu\text{g.L}^{-1}$ heavy metals, in the filtrate after separation from the solids, and of the filters after redissolution in 1.5M HNO_3 , calculated back to the original 500ml start solution.

	$\text{PO}_4\text{-P}$	$\text{NH}_4\text{-N}$	Mg	As	Cd	Co	Cr	Cu	Ni	Pb
	mg.L^{-1}			$\mu\text{g.L}^{-1}$						
Limit of quantification	1	1	1	1.4	0.2	0.2	0.4	0.9	0.6	1.5
Initial conc. in hydrolysed urine	228 (± 1.5)	4646 (± 86)	0.6 (± 0.07)	151 (± 4.0)	5.0 (± 0.2)	13.8 (± 1.4)	11.0 (± 0.4)	88.4 (± 5.6)	8.1 (± 2.2)	27.2 (± 1.6)
After spiking with 100 $\mu\text{g.L}^{-1}$ heavy metals				248 (± 19.1)	84.5 (± 13.7)	94.4 (± 9.0)	97.8 (± 2.8)	168 (± 24.5)	95.4 (± 3.3)	98.4 (± 13.7)
Filtrate	2.4	4272 (± 1.5)	70 (± 1.5)	251 (± 6.0)	20.8 (± 3.5)	55.7 (± 3.7)	86.5 (± 6.0)	85.6 (± 19.9)	81.8 (± 4.6)	60.4 (± 8.3)
Remaining in solution				101%	25%	59%	88%	51%	86%	61%
Filter residue	191	208	184	49.9	46.1	35.0	21.0	78.5	23.8	61.8
Precipitating				20%	55%	37%	21%	47%	25%	63%

Between brackets the standard deviations of 3 urine and 4 filtrate samples are given.

As expected from the earlier batch experiments (Figure 4-1), the elements cadmium, copper and lead do precipitate substantially together with struvite formation. Of these metals, between 47%

and 63% can be found in the solid phase. For the other metals between 20 and 37% precipitation is found.

4.4.2.4 Discussion of the heavy metal experiments

The chemical conditions of stored and therefore hydrolysed urine influence not only the solubility of magnesium and calcium (Udert *et al.*, 2003b) but also of other metals. Thermodynamic considerations show that Cd, Co, Cr, Cu, Ni and Pb can potentially precipitate as carbonate or hydroxides with low or very low equilibrium concentrations. We could show the actual precipitation of Cd, Cu and Pb in stored urine with a reaction half-life of approximately 7 days.

During struvite precipitation in urine with elevated metal concentrations, between 20% and 63% of the added heavy metals were found in the solid phase. A clear difference was observed between metals that precipitate spontaneously in stored urine (47% to 63%) and the metals that do not (20% to 37%). Due to the fact that heavy metals were added to the urine in concentrations above thermodynamic equilibrium, it can be assumed that these co-precipitation ratios represent upper limits for heavy metal incorporation into struvite.

Average heavy metal concentrations determined in collected urine are given in Table 4-7. The comparison with commercial fertiliser and manure shows that specific heavy metal concentrations (heavy metals per unit of nitrogen or phosphorus) in urine is generally low, mostly far below that of available fertiliser. E.g., agricultural bulk fertiliser analysed by Rogowski *et al.* (1999) contains a cadmium concentration of 11.5 mg Cd gP⁻¹, which is several orders of magnitude higher than the 0.007 mg Cd kgP⁻¹ average found in urine (Table 4-7). Our measured concentrations are in good agreement with data previously reported in literature.

Table 4-7: Heavy metal concentrations measured in urine.

Source:	Concentrations							Specific concentrations					
	Urine							Urine		Fertiliser		Manure	
	[1a]	[1b]	[1c]	[2a]	[2b]	[3]	[4]	µg×gP ⁻¹	µg×gN ⁻¹	µg×gP ⁻¹	µg×gP ⁻¹	µg×gN ⁻¹	µg×gP ⁻¹
Cd [µgCdL ⁻¹]	0	0.3	5.0	0.2	0.2	<1	3.0	6.9	0.4	41	11.5·10 ³	16.1	25
Cr [µgCrL ⁻¹]	3.9	4.2	11.0	2.0	4.0	19	6.4	29.2	2.2	415	38.5·10 ³	57	573
Co [µgCoL ⁻¹]	2.5	2.9	13.8	1.0	12.0	<5	0.6	31.4	2.0	21	1008	3.1	311
Cu [µgCuL ⁻¹]	243	50.9	88.4	155	155	2.5	23.2	387	33.6	20	-	-	17.3·10 ³
Ni [µgNiL ⁻¹]	5.8	3.1	8.1	15	227	61	2.0	288	22.8	100	17.0·10 ³	23.8	996
Pb [µgPbL ⁻¹]	14.2	15.5	27.2	2.0	2.0	<10	35.2	45.4	2.9	29	2648	6.2	274
Zn [µgZnL ⁻¹]	537	229		110	70	200	336	667	50.0	410	157·10 ³	390	23.8·10 ³
Al [µgAlL ⁻¹]	244	197		210	185		-	1168	66.5	-	-	-	-
Fe [µgFeL ⁻¹]	116	125		205	165		68.9	654	44.2	-	-	-	-

The specific concentrations (i.e. the metal concentration relative to the phosphorus and nitrogen content) in urine are averaged for all sources (for [4] a P/N-conc. of 800gPm⁻³ / 9000gNm⁻³ was assumed). The values for [5] are the median from 4 agricultural and 11 home-use fertilisers. Legend: [1 a, b, c] measured urine concentrations from 3 independent samples, [2]: Kirchmann and Pettersson (1995) (a, b different locations), [3]: Jönsson *et al.*, 1997), [4]: Ciba-Geigy (1977), [5]: McBride and Spiers (2001), [6]: Rogowski *et al.* (1999).

The experiments show that the precipitation processes during urine storage (mainly struvite, Udert *et al.*, 2003b) would reduce the specific heavy metal content even more. Elevated concentrations of Cd, Cu and Pb, e.g. due to the use of corresponding piping material would be eliminated during storage and end up in the 'urine sludge'.

The measurement of struvite without addition of heavy metals did not yield any detectable concentrations. Eight struvite samples, obtained by precipitation from non-spiked urine as described

in Ronteltap *et al.* (2007a), were re-dissolved in 25ml 1.5M HNO₃. The obtained solutions contained 0.99-2.63g struvite.L⁻¹ or 0.22-0.60g PO₄-P.L⁻¹. None of the determined heavy metals was present above the detection limits as given in Table 4-6.

Thus, typical heavy metal elimination via struvite precipitation does not exceed 6.4 µg As, 0.9 µg Cd and Co, 1.8 µg Cr, 4.1 µg Cu, 2.7 µg Ni and 6.8 µg Pb per g PO₄-P. These specific concentrations are significantly lower than the typical specific concentrations found in stored urine (Table 4-7).

4.5 Conclusions

In this paper, the behaviour of pharmaceuticals, hormones and heavy metals during struvite precipitation in source-separated urine was studied. The main conclusions are:

- During struvite precipitation, hormones as well as pharmaceuticals (non-ionic, acidic and basic) remain in solution for > 98 %.
- The introduction of a washing step after filtration results in a slightly cleaner product.
- The chemical conditions of stored and, therefore, hydrolysed urine influence the solubility of dissolved metals. Thermodynamic considerations show that cadmium, cobalt, chromium, copper, nickel and lead potentially precipitate as carbonates or hydroxides resulting in low or very low equilibrium solute concentrations. We were also able to show Cd, Cu and Pb precipitation in stored urine with a reaction half-life of approximately 7 days.
- During struvite precipitation between 20% and 63% of the added heavy metals were found in the solid phase. Higher values (47% to 63%) were found for the metals that precipitate spontaneously in stored urine, whereas for the others fractions between 20 % and 37 % were determined.
- For optimal phosphate recovery as pure struvite it is important to minimize the amount of phosphate precipitating already during storage, by minimizing the amount of flush water that contains magnesium and calcium.
- For As, Cd, Cr, Co, Cu, Ni, Pb, Zn, Al and Fe the maximum specific metal concentrations per gram P or N are mostly lower in urine than in commercially available fertilisers and manure.
- Struvite precipitated from normal stored urine had heavy metal concentrations below the detection limit (1.4 µg As L⁻¹, 0.2 µg Cd L⁻¹, 0.2 µg Co L⁻¹, 0.4 µg Cr L⁻¹, 0.9 µg Cu L⁻¹, 0.6 µg Ni L⁻¹, 1.5 µg Pb L⁻¹). With specific heavy metal concentrations of 6.4µg As, 0.9 µg Cd and Co, 1.8 µg Cr, 4.1 µg Cu, 2.7 µg Ni and 6.8 µg Pb per g PO₄-P, these are significantly lower than the typical specific concentrations found in stored urine, indicating that only a small fraction of the metals in urine is attached.
- Phosphate recovery from urine via struvite precipitation yields a product that eliminates most of the organic micropollutants and contains only a fraction of the already low amounts of heavy metals in urine.

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**Struvite precipitation from urine - influencing factors
on particle size**

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Abstract

Struvite crystallisation is a fast and reliable phosphorus removal and recovery process for concentrated waste streams – such as hydrolysed human urine. In order to optimise P-elimination efficiency, it is beneficial to obtain larger particle sizes: they are easier to separate and less prone to wash-out than smaller particles. This paper presents the results of a study on the effect of process parameters on particle size in a single step struvite precipitation. Crystals formed in batch experiments with real hydrolysed urine were shown to have an average size of $> 90 \mu\text{m}$ at pH 9 and 20°C . This is reduced to $45 \mu\text{m}$ when changing stirrer type. Particle size increases with lower supersaturation. The results showed that under otherwise constant conditions, particle size decreases with lower temperature and has a minimum between pH 9 and 10. Deviating trends are observed at $\text{pH} < 8$. Struvite formation in a CSTR process was shown to be a reliable stable process that does not require any pH control. A method based on conductivity measurement is presented to estimate ionic strength, which is needed for equilibrium calculations.

Keywords struvite, urine, phosphorus recovery, crystal size, supersaturation

5.1 Introduction

The concern for diminishing phosphorus reserves are being expressed progressively. Supplies, particularly for high-grade phosphate ores, were reported low over 2007 and continuing into 2008, leading to drastic price increases (U.S. Geological Survey, 2009). Phosphorus demand is projected to increase even further with a global peak in phosphorus production predicted to occur around 2030 (Cordell *et al.*, 2009). Phosphorus is not only indispensable for a secure food production to feed an increasing world population. The growing production of crops for bio fuel production places an additional burden on the global P reserves. At the same time, phosphorus forms a problematic waste stream in those areas where there is no adequate wastewater treatment, or is responsible for extra costs when it needs to be disposed of in landfills as incineration ash. In view of a more sustainable future, we need to look at alternative sources of phosphorus. In other words, we need to recycle.

Within conventional wastewater treatment, several pathways are known to remove phosphorus out of the wastewater; the recovery product then being a phosphorus-rich water or sludge stream. Within the concept of wastewater design, we find a stream that is very low in volume, yet very high in phosphorus: human urine. A technique proven to be a successful method to recover phosphorus from high strength phosphorus-rich streams is the precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (Battistoni *et al.*, 2000; Kabdaşlı *et al.*, 2006). Struvite is a known and applied slow-release fertiliser, well applicable to crops in soils with relatively low pH. For plants that need an initial high dose of P followed by a continued slow P release, for example container plants, a product called *enhanced struvite* is already on the market: struvite treated with phosphoric acid to achieve a modified form of DAP (dimagnesium phosphate, one of the most applied fertilisers in the world) (Gaterell *et al.*, 2000). Shu *et al.* (2006) showed that phosphorus recovery in the form of struvite is technically feasible and economically viable.

Many research groups studied the behaviour of struvite, in different types of waste streams (Battistoni *et al.*, 2000; Burns *et al.*, 2001; Jaffer *et al.*, 2002), and already some full scale reactors are in operation (Ueno and Fujii, 2001). They mainly treat the process water from industries to prevent problems and/or costs further down the process stream (Moerman *et al.*, 2009). Lab studies on

struvite formation have been performed in urine as well (Ganrot *et al.*, 2007; Ronteltap *et al.*, 2007a). However, urine forms a special waste stream in that sense that it has a high salt concentration, a very high buffer capacity, and a high concentration and special combination of dissolved and suspended organic material. To accommodate the process of upscaling the lab reactors, more specific knowledge on the effect of process parameters for a system run with urine is important.

In this paper, we study the effect of process parameters on crystal size and phosphorus recovery efficiency. We give some indications, which parameters affect particle size in a single step struvite precipitation. Knowing these effects will facilitate the implementation and understanding of struvite precipitation from urine on a bigger scale.

5.2 Material & Methods

5.2.1 Urine, reagents and stock solutions

Hydrolysed human urine was used as influent for the continuous reactor. Real urine was collected from the storage tank installed at the No Mix toilet facilities at the Eawag research institute in Duebendorf, Switzerland (Ronteltap *et al.*, 2007a). At the time of applying the urine in the experiments, the urea was fully hydrolysed due to microbial urease. Table 5-1 shows the start concentrations of ammonium and phosphate and the pH values.

Table 5-1: Average values and standard deviations (std) of initial ammonium and phosphate concentrations and pH value, for reactor and batch experiments.

Experimental set-up	PO ₄ -P	(NH ₄ +NH ₃)-N	pH
Reactor experiments	217 ± 19.8 std	4591 ± 85.3 std	9.05 ± 0.11std
Batch experiments	241 ± 15.0 std	5059 ± 194.5 std	8.94 ± 0.02std*

* For the batch experiments with varying pH, the pH was adjusted as described in the text

Magnesium was added as magnesium chloride, either in powder form or as a magnesium solution of typically 0.49 M (99.76 g.L⁻¹ MgCl₂·6 H₂O). This led to a typical Mg:P ratio of 1.5. Due to the hygroscopic nature of magnesium chloride, the concentrations in all stock solutions were checked with ion chromatography. In order to stop the crystallization process in the vials, samples for phosphate-, ammonium- and magnesium analysis were prepared as follows: the samples were filtered over Whatman glass fibre GF/F filters (average pore size 0.7µm), acidified with 2 M hydrochloric acid (HCl_{aq}) and stored in PE plastic containers at 4°C until analysis. For size measurements with a Mastersizer X (Malvern Instruments Ltd., Worcestershire, United Kingdom) a saturated struvite solution was composed of 1.31 g disodium hydrogen phosphate (Na₂HPO₄), 1.6 g magnesium chloride (MgCl₂·6H₂O) and 0.86 ml 25% ammonia solution in 1 litre deionised water. The solution was decanted carefully from the precipitates and filtered. Adjustment of the pH was conducted with 10 M sodium hydroxide (NaOH) and hydrochloric acid (HCl_{aq}) solutions. All chemicals used were analytical grade and originated from Merck (Switzerland).

5.2.2 Reactor (CSTR) set-up

Urine was taken from the collection tank in transportable 20 litre jerry cans. Particulate material was allowed to settle in the jerry cans which were used for influent storage. The glass precipitation vessel contained a liquid volume of 1.1 litre with additional head space. Influent was continuously pumped into the reactor at a rate of 88 ml.h⁻¹ through silicone tubes. Magnesium chloride solution was added

at 12 ml.h⁻¹, leading to an average molar Mg:P ration of 1.33. A magnetic stirrer was used for mixing. Liquid and crystals leave the reactor via an overflow to a settling zone, consisting of a plastic funnel with wide outflow. Periodically, the sedimented particles were released by opening a valve at the bottom of the settling zone. The supernatant overflowed to a 20 litre effluent collection tank. The reactor was operated as a simple flow through reactor with no recirculation (CSTR), with a solid and hydraulic retention time in the reactor of 11 hours. Each new influent tank was sampled and analysed for pH, ammonium and phosphate. When replacing the effluent tank, the effluent was stirred well and samples were collected for analysis.

5.2.3 Supersaturation calculations

In our experiments, we apply different conditions to struvite precipitation by adding magnesium chloride to hydrolysed human urine from a collection system and assessed the effect of process parameters on particle size. Crystal formation is a process in which many aspects play an important role: thermodynamics (solubility), mixing effects during the experiment, nucleation, mass transfer phenomena between the liquid phase and the surface, mechanical stability of the crystals and of course crystallisation kinetics. Most of these processes can be quantified by using supersaturation as a parameter. Supersaturation is the degree in which the solute concentration deviates from its equilibrium in a given solution. For struvite, supersaturation β is defined as:

$$\beta = \frac{f_1 \cdot [NH_4^+] \cdot f_2 \cdot [Mg^{2+}] \cdot f_3 \cdot [PO_4^{3-}]}{K_s^0} \quad (5-1)$$

where $[NH_4^+]$, $[Mg^{2+}]$ and $[PO_4^{3-}]$ are the concentrations of NH_4^+ , Mg^{2+} and PO_4^{3-} , f_1 , f_2 and f_3 their activity coefficients and K_s^0 is the standard solubility product (Stumm and Morgan, 1996).

5.2.4 Particle size experiments

In order to identify parameters that affect struvite crystal size, we conducted several batch experiments. The experiments were carried out in a double walled, temperature controlled glass reactor with either a magnetic or propeller stirrer. Unless stated otherwise, the runs typically were performed with 1 L urine and lasted 75 minutes; the 25 ml of 0.49 M magnesium chloride was added via a burette constantly over the period of 75 s. Crystal size measurements were performed at different times (typically after 15, 30, 45, 60 and 75 min.) with a Mastersizer X (Malvern Instruments Ltd., Worcestershire, United Kingdom). Measurements were based on the principle of laser ensemble light scattering; the results are given as the average of 5000 sweeps (10 s measurement time). Before each measurement, the suspension chamber of the sensing zone and the connecting tubes were rinsed and filled with a saturated struvite solution, which was also used as the carrier medium to flush the sample through the measurement chamber. Batch experiments were carried out in the proximity of the Mastersizer, so that samples could be measured directly. For experiments with more than one analysis the standard deviation or σ is given, calculated as the square root of the variance. Average sizes indicate an average over the size measurements over time (typically 15, 30, 45, 60 and 75 min.). These measurements themselves are the average of 3 analyses, carried out by the Mastersizer X. Samples for magnesium, ammonium and phosphate analysis were taken, acidified and stored cool at 4°C until analysis. Calcium was not analysed since it was shown before that hydrolysed urine contains only very limited concentrations (Ronteltap *et al.*, 2007a).

5.3 Results

5.3.1 Effect of pH and temperature on crystal size

5.3.1.1 Reproducibility and influence of experimental time

Initial experiments were carried out to identify the experimental duration needed to achieve stable particle sizes and to check reproducibility of the measurements. To 0.5 litre hydrolysed urine, stirred with a magnetic stirrer, magnesium chloride was added in powder form at a Mg:P ratio of 1.5. Samples were taken after 15, 30, 45, 60 (and 75) minutes for particle size distribution measurements. Figure 5-1 shows 7 similar experiments with average particle size over time.

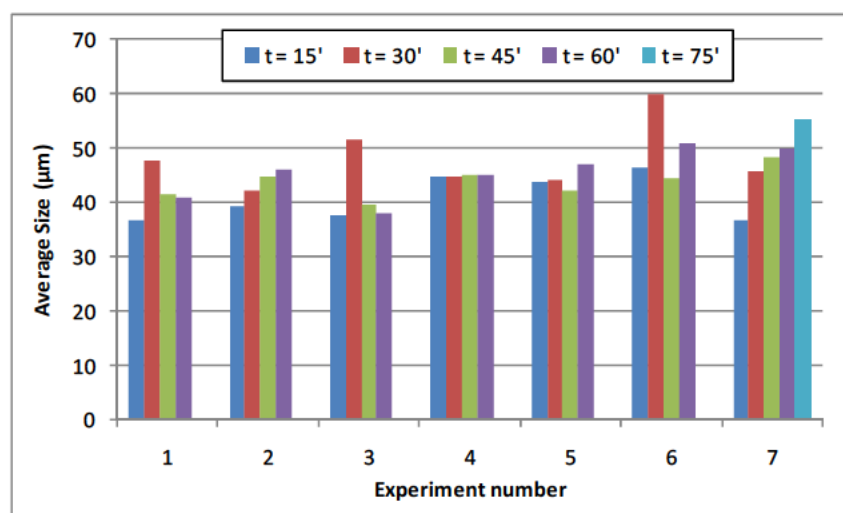


Figure 5-1: The course of particle size distribution for struvite crystals in hydrolysed urine at room temperature (20°C).

There is no significant time dependent shift recognisable in particle size. Using these 7 experiments, each with 4 (5 in experiment 7) independent measurements, we get a standard deviation of 5.4 µm (12.0%) at an average particle size of 44.8 µm (n = 29). Figure 5-2 shows the results of one typical experiment, running over 125 minutes. The inset graph presenting mean particle sizes shows that within the estimated experimental standard deviation, the particle solution can be viewed as stable over the entire period. Due to the larger volume needed, the experiment was conducted slightly different (2.5 L volume with similar stirrer and a molar magnesium to phosphate ratio of 1.5) than the ones described above. Therefore, the average particle sizes are not directly comparable. Samples taken after 2 minutes confirm that chemical equilibrium is reached in a short period of time (Ronteltap et al., 2007a).

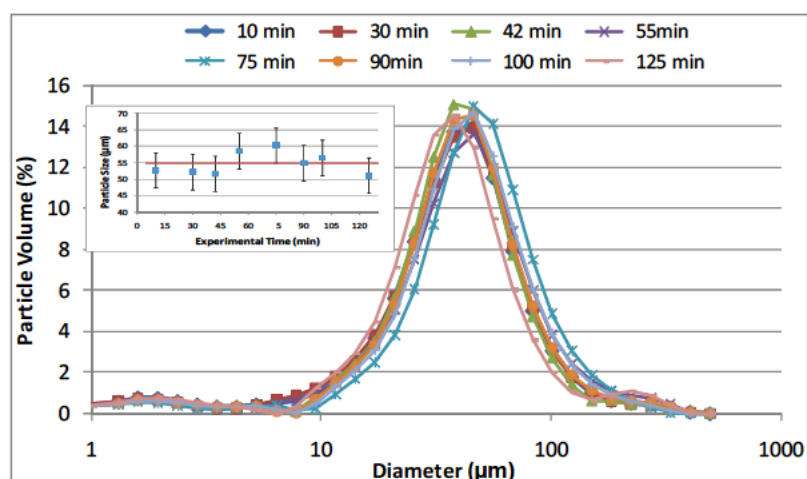


Figure 5-2: Particle size distribution for one experiment (#8) and 8 measurements between 10 and 125 minutes. (MgCl₂·6H₂O) added as powder, stirred with a magnetic stirrer at room temperature, 20°C; 2.5 L total volume.

5.3.1.2 Filtration of urine

Other researchers have experimented with struvite precipitation in the presence of seeding material (Battistoni *et al.*, 2002, Suzuki *et al.*, 2005, Wang *et al.*, 2006) in order to improve phosphorus recovery. In the presence of seed material, nucleation can take place on the seed surface which might influence crystal size (Shimamura *et al.*, 2003). We tested the effect of natural seeding in our system by comparing struvite precipitation in filtered and unfiltered urine. Unfiltered hydrolysed urine contains particles between 1.6 – 1.95 μm (Figure 5-3, left), which could serve as nuclei surfaces. Yet, upon addition of magnesium to both GF/F filtered and unfiltered hydrolysed urine, we did not find a difference in crystal size (Figure 5-3, right). The experiment was performed in triplicates with each four independent particle size measurements; the results are listed in Table 5-2. Nevertheless, subsequent experiments were carried out with filtrated (GF/F) urine.

Table 5-2: Struvite precipitation carried out threefold with filtered urine; stirrer: magnetic.

Exp.	Average crystal size (μm)			
	15'	30'	45'	60'
i	37.7	51.6	39.5	37.8
ii	44.9	44.7	45.1	45.1
iii	43.9	44.0	42.1	47.1
Overall	43.6 (σ = 3.9)			

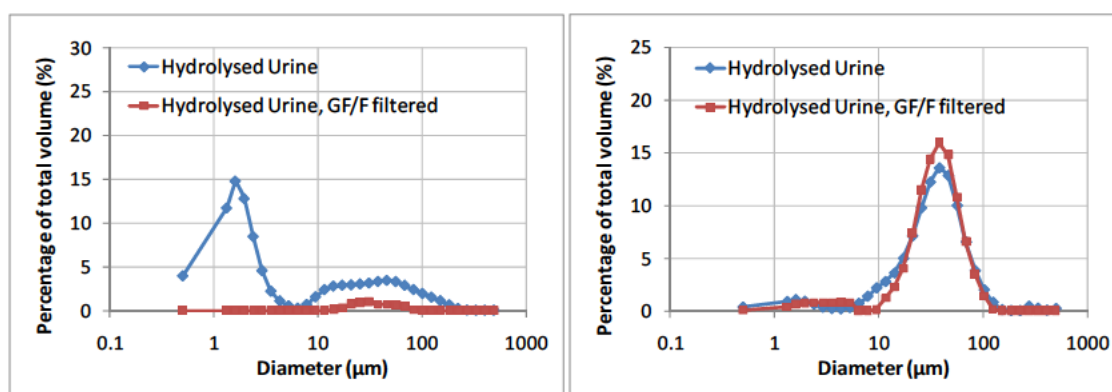


Figure 5-3: Particle size distribution in filtered and unfiltered urine, before (left) and after magnesium addition (right). The peak between 1.6 and 1.95 μm was verified by adding a particle-standard (37.8±0.5 μm) in order to increase the signal to noise ratio (results not shown). The broad peak between 10 and 100 μm however is most probably an artefact of the low signal to noise ratio. Stirrer: magnetic.

5.3.1.3 Type of stirrer

To test the effect of the stirrer, we compared two types: a magnetic stirrer and a two-blade propeller, operated at approx. 300 rpm. Figure 5-4 shows clearly the strong influence of the stirrer on the particle size. The average size increases from 45 μm ($\sigma = 1.4 \mu\text{m}$, $n = 8$) in experiment 9 and 10 to 92 μm ($\sigma = 1.1 \mu\text{m}$, $n = 8$) in experiment 11 and 12. In all following experiments, the two-blade propeller was used for stirring.

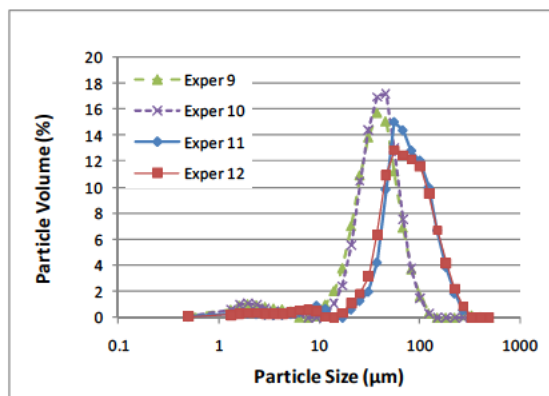


Figure 5-4: Crystal size distribution obtained with magnetic stirring (exper. 9 and 10) and a propeller stirrer (exper. 11 and 12). The average particle size increases from 45 to 92 μm .

5.3.1.4 The effect of pH on struvite formation

We measured the precipitant concentration and crystal sizes during struvite precipitation experiments at pH values ranging from 7 to 11, using the propeller stirrer. All other experimental conditions are described in Material & Methods. Table 5-3 lists the results from experiments 13 to 19. Figure 5-5 shows the average crystal size (typically $n=4$) as a function of pH.

Table 5-3: Crystal size, removal efficiency and supersaturation at tested pH values. Typical P_{influent} was 240 mg P.l^{-1} ; stirrer type propeller.

Operational conditions					Crystal Size		Phosphorus removal		Degree of supersaturation
Exp. nr.	pH	T °C	Mg/P	Mg addition	Average μm	σ μm	Effluent mgP/L	Efficiency %	
13	7	25	1.5	solution	74	12.0	17.6	92.2	1.16
14	7.5	25	1.5	solution	126	20.0	13.2	94.1	1.85
15	8*	25	1.5	solution	136	22.8	6.2	97.3	2.11
16	8.5	25	1.5	solution	121	3.9	3.5	98.4	2.52
17	9	25	1.5	solution	92	0.7	1.4	99.4	2.87
18	10	25	1.5	solution	90	0.7	1.4	99.4	2.78
19	11	25	1.5	solution	129	8.1	1.2	99.5	2.21

*Average of 2 experiments

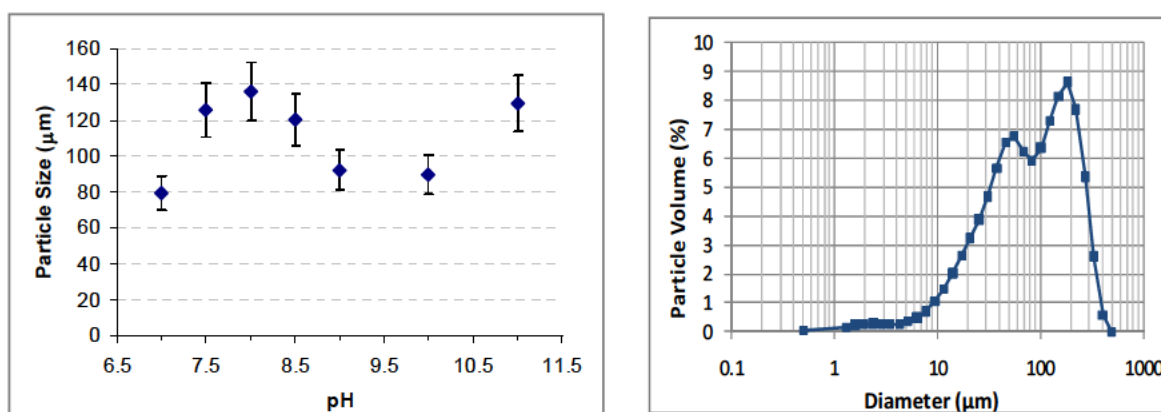


Figure 5-5: Average crystal size as a function of pH - the error bars indicate the relative standard deviation estimated from experiments 1 - 7 (left). Right: particle size distribution for experiment 19 at pH 11. See Table 2 for experimental conditions.

5.3.1.5 Temperature

A comparable set of experiments was carried out at constant pH 9 and different temperatures (Table 5-4). All other experimental conditions were similar like in experiments 13 to 19 and described in Materials & Methods. The solubility was calculated with the Van't Hoff equation (Stumm and Morgan, 1996), the standard solubility of struvite at 25 °C of $10^{-13.26}$ M³ and the estimated formation enthalpy of struvite ΔH 22.6 (\pm 1.1) kJ.mol⁻¹ (Ronteltap *et al.*, 2007a). Figure 5-6 shows the average crystal size (typically n=4) as a function of temperature.

Table 5-4: Crystal size, removal efficiency and solubility at tested temperatures

Exp. nr.	Operational conditions				Crystal Size		Phosphorus removal		Struvite Solubility pKs,0
	T °C	pH	Mg/P	Mg addition	Average μm	σ μm	Effluent mgP/L	Efficiency %	
20	5	9	1.5	solution	62	0.7	0.9	99.6	13.54
21	10	9	1.5	solution	66	1.3	1.1	99.5	13.47
22	20	9	1.5	solution	93	1.4	1.5	99.3	13.33
23	25	9	1.5	solution	92	0.7	1.4	99.4	13.26
24	30	9	1.5	solution	102	1.4	2.1	99.1	13.19

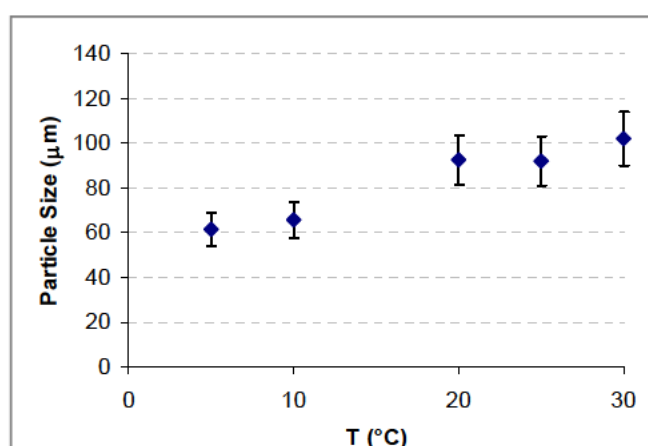


Figure 5-6: Average crystal size as a function of temperature. The error bars indicate the relative standard deviation estimated from experiments 1 - 7.

5.3.2 Morphology of struvite crystals

Published morphology types range from coffin-like (Wierzbicki *et al.*, 1997) and needle-like (Abbona and Boistelle, 1985) to trapezoidal (Münch and Barr, 2001). All of these forms are described as “typical for struvite”. In our experiments we found mainly x-shaped branched crystals (Figure 5-7 left). Only at the experiment with high pH (experiment 19, pH 11) the morphology changed to a more dendrite-like shape (Figure 5-7 middle). With Scanning Electron Microscopy, we were able to zoom in better on individual crystals (Figure 5-7 right).

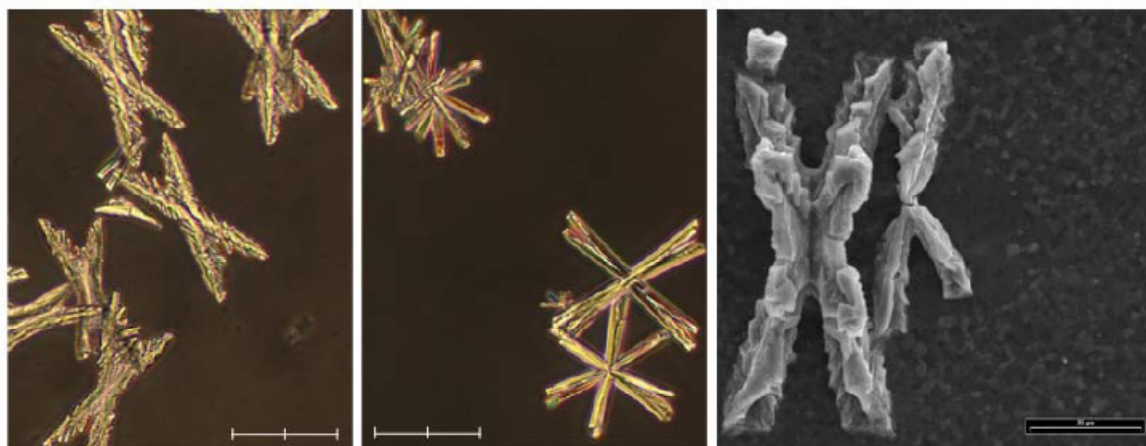


Figure 5-7: Microscopic pictures of struvite crystal morphology: light microscopy at pH 10 (left); light microscopy at pH 11 (middle); Scanning Electron Microscopy of crystals produced in the reactor at pH 9 and 20°C (right). The measure bars on the left and middle indicate 50 µm; on the right 20 µm.

5.3.3 Results from continuous struvite precipitation reactor

5.3.3.1 CSTR performance

In a system used for micropollutant inclusion experiments (Ronteltap *et al.*, 2007b) the possibility of continuous struvite production was observed. In Figure 5-8 the performance of the lab reactor is shown. From the moment of start-up, the removal of phosphorus from the reactor was high. The total average removal was 98.7 %. On day 58 the magnesium tube clogged, causing increased P concentrations in the effluent. When leaving out the measurements of that particular effluent tank with elevated P concentration, the average is 99.0%, at a Mg:P ratio in the influent of 1.33 ± 0.06 . The crystals formed in the reactor had an average median diameter of 91 µm. These results are very similar to those obtained by the batch experiments.

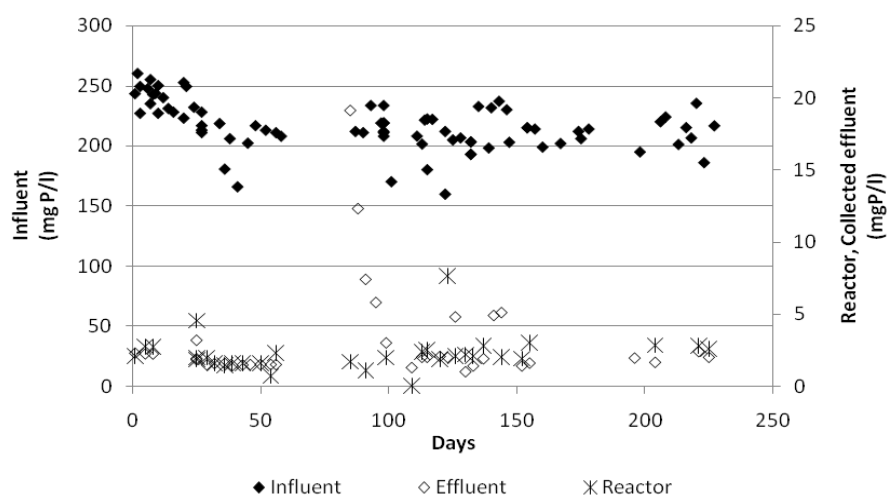


Figure 5-8: Ortho-phosphate concentrations of influent, collected effluent and the continuously stirred reactor over the period of investigation, i.e. 227 days.

Some operating aspects of the continuous reactor:

- Drying of the product: periodically (every 4 - 5 days), approximately 100 ml of the sedimented crystals were discharged by manually opening a valve. The crystals formed a thick slurry, with a dry weight content of 65 %. Drying in an oven for 2 days at 30 °C increased this to 99%. Complete evaporation can also be achieved by air drying (Münch and Barr, 2001). The obtained crystals form one entity which can be ground easily into a fine white/grey, odourless powder.
- Excess ammonium: in the reactor influent, the molar ammonium to phosphate ratio was on average 51.8, a normal value for stored untreated urine. An excess of ammonium was reported to be beneficial for struvite precipitation, mainly by providing a good pH buffer (Stratful *et al.*, 2004).
- Scaling in the reactor: on the walls of the glass reactor as well as on the magnet stirrer a layer of struvite formed very soon after start-up (visible after a few days). After the run time (227 days) we emptied the reactor and found scaling on the walls as well as a 2 cm deposit of struvite formed on the bottom around the radius of the magnetic stirrer.

5.3.4 Practical issues for struvite precipitation from urine

5.3.4.1 Conductivity as a measure for ionic strength and dilution factor

Urine from a collection system can vary in concentrations. This is due to: (i) Differences in human water consumption and nutrition that can lead to concentration variations, (ii) Depending on the collection system, flush water may end up in the collected urine.

The degree of dilution can be determined with the dilution factor, defined by Udert *et al.* (2003). The dilution factor is obtained by comparing the measured ammonia concentration to the standard value of 8 gN.L⁻¹. Another approach is to make use of the relation between dilution and conductivity. Conductivity is reduced upon dilution. Yet, due to the many different interactions between the ions, the reduction is not necessarily linear. In order to study the relation between conductivity and the dilution factor, we measured conductivity in hydrolysed urine. The initial conductivity of the urine in the storage tank was 36 mS.cm⁻¹ at 20.7°C. This hydrolysed urine taken from the storage tank had already undergone a certain dilution due to some flush water. The initial dilution factor of 1.68 was

derived by comparing the ammonium concentration with the standard value of 8 gN.L^{-1} (Udert *et al.*, 2003). The urine was then diluted with tap water while registering the change in conductivity (Figure 5-9). Conductivity was measured using a WTW 330i handheld conductivity meter with non-linear temperature correction. A calibration curve was obtained between conductivity and ionic strength (Figure 5-9). In the tested range the curve is close to linear.

Since conductivity is also related to concentration of dissolved species, ionic strength was added to the calibration curve. The ionic strength was estimated by letting the model as described in Ronteltap *et al.*, 2007b mix hydrolysed urine with tap water in PHREEQC (Parkhurst and Appelo, 1999), in the applied ratios. For the composition of tap water at Eawag the concentrations given in Udert *et al.* (2003) were used. With this calibration curve, conductivity measurements can be used to estimate ionic strength, for solutions equal to fully hydrolysed urine with respect to ionic composition.

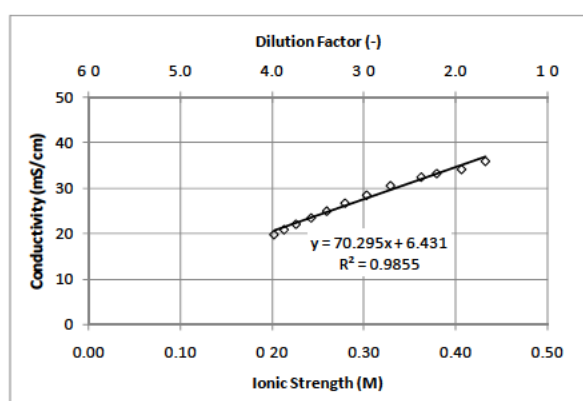


Figure 5-9: Conductivity as a measure for ionic strength. Such a calibration curve can be used to determine the ionic strength in solutions equal to fully hydrolysed urine with respect to ionic composition, and makes the elaborate calculation of ionic strength redundant.

5.4 Discussion

5.4.1 Mixing

In the used experimental set-up, nucleation can be considered fast and spontaneous. All investigated concentrations are consistent with equilibrium concentrations. The experiments with the different mixer types indicate that due to the fast nucleation reaction, mixing is an important precipitation parameter. Low turbulences and therefore slower dissipation of precipitants lead to locally higher supersaturation preferring nucleation over crystal growth (Mersmann, 2001). This would explain the smaller crystal sizes achieved with the magnetic stirrer compared with the more powerful propeller stirrer (Figure 5). We did not investigate the detrimental effect of high turbulences on crystal size. In Figure 5 the form of the size distribution (dip in the peak region) of the propeller stirred experiments look like first signs of decay of larger crystals. However, this visual effect in the size distribution is not a generic observation. More investigations need to be done in order to optimise mixer energy inputs for struvite formation.

5.4.2 Heterogeneous nucleation

Urine from collection systems contains particles between $1.6 - 1.95 \mu\text{m}$. Eliminating these particles does not change the particle size distribution significantly (Figure 5-3 right). This shows that these

particles do not serve as an important source for heterogeneous nuclei. Comparable experiments with artificial urine (recipe according to Udert *et al.*, 2003) show with 65 μm (standard deviation σ : 5.7 μm , 2 experiments with each $n = 4$; results not shown) a clearly higher average particle size than the measured 45 μm (σ : 5.4 μm). There are several reasons why inorganic artificial urine might show different precipitation behaviour. Nevertheless, it cannot be excluded that storage conditions might influence the precipitation of struvite.

5.4.3 Temperature and pH

Temperature and pH have a direct influence on the solubility of struvite and therefore on the thermodynamic properties (Ronteltap *et al.*, 2007a). Under otherwise constant precipitation conditions, changes in pH and temperature lead to a direct change of the supersaturation during the precipitation process. Figure 10 shows the theoretical supersaturation at the very beginning of the pH experiments, assuming perfect mixing conditions. The values were estimated with PHREEQC (Parkhurst and Appelo, 1999) and the model described in Ronteltap *et al.* (2007b). Because the experimental conditions remain constant (except pH), the results of the calculations shown in Figure 10 serve as a proxy for the effective supersaturation at the beginning of the precipitation.

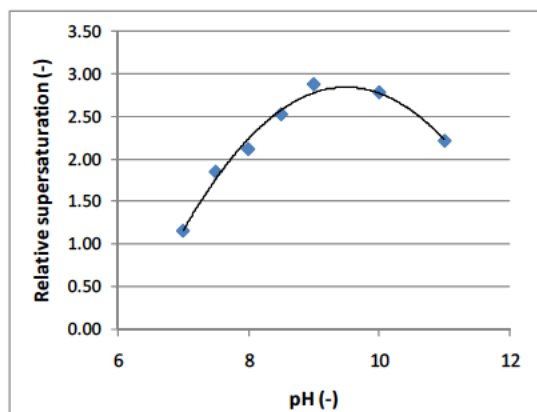


Figure 5-10: Theoretical relative supersaturation estimated with PHREEQC, at the very start of pH experiments. The line provides visual aid only.

The maximum supersaturation is reached between pH 9 and 10, which corresponds well with the minimum in particle size (Figure 5-5 right).

A similar effect can be identified in the temperature experiments. Table 5-4 shows that at lower temperature the solubility decreases, which has according to equation (5-1) an increased supersaturation as a consequence. This leads to the decrease in particle size, visible in Figure 5-7. An exception is the measured particle size at pH 7, which does not confirm the otherwise systematic trend. This might indicate a change in precipitation kinetics, e.g. due to a change of the surface charge, influence of the chloride added for pH control or because of a surface controlled effect by the increased concentration of dihydrogen phosphate (H_2PO_4^-). Similarly, at pH 11 the visual observations of the crystal shapes (Figure 5-7) indicate that at high pH the precipitation processes change. This is also supported by the particle size distribution, which shows a double peak only for pH 11 (Figure 5-5, left). Although XRD analysis in previous studies confirmed 100% struvite formation from urine at pH 9 (Ronteltap *et al.*, 2007a), there is no XRD confirmation that at other pH values solely struvite is formed.

5.4.4 Particle size

The results show that changes in supersaturation have a direct influence on the average particle size. Higher supersaturation, either by weak mixing, pH at the minimal solubility, or low temperature leads to smaller particle sizes. This can be explained by the competition between nucleation and crystal growth. At high supersaturation, the nucleation rate is higher, which leads to the formation of more and therefore smaller crystals (Mersmann, 2001). The rather high initial magnesium to phosphorus ratios in the reactor and batch experiments lead to relatively high initial supersaturation conditions. Although the effects of varying parameters were well distinguishable with these initial conditions, the effects may have been more pronounced at lower initial magnesium to phosphorus ratios.

The particle sizes from the batch experiments of 92 and 93 μm (pH 9 and 20 °C) corresponds with the 110 μm reported by Münch and Barr (2001) in anaerobic side streams. Le Corre *et al.* (2006) showed that struvite particle size is limited due to the zeta-potential of struvite. Because of their negative zeta-potential, the crystals do not agglomerate. It was shown that a higher pH leads to a larger negative zeta-potential, which leads to reduced particle sizes. This indicates that under the typical conditions in hydrolysed urine larger crystals cannot easily be formed and thus the particle sizes we obtained are typical for struvite precipitation in urine.

5.4.5 CSTR performance

The reactor showed very stable operation conditions and high removal efficiencies. The main advantage of using urine as a source for struvite precipitation is that no pH adjustment is needed. This allows for a stable running of the reactor without operation issues for a longer period of time, provided magnesium is supplied sufficiently.

The crystal size of 91 μm found in the reactor however corresponds well with the results obtained at low supersaturation. Although the CSTR was agitated with a magnetic stirrer instead of a propeller, the effective supersaturation in the reactor was low due to the continuous precipitation. This confirms earlier results regarding the dependency of particle size on supersaturation.

5.4.6 Phosphate elimination

The P-elimination efficiencies in most experiments and in the CSTR exceeded 98% - exceptions are the experiments done at low pH values. This corresponds well with the expected solubility of struvite. Similar results were reported by Kabdaşlı *et al.* (2006). Ronteltap *et al.* (2007a) showed that the solubility depends strongly on the ionic strength or dilution, respectively. For a first estimation of the ionic strength of urine with a known dilution, Figure 5-9 can give preliminary information. Dilution of urine has another substantial effect on P-elimination efficiency. The larger the dilution, the more phosphate is remaining in solution, due to the fact that the endpoint of precipitation is defined by equilibrium concentrations. On the offset, higher dilution and lower ionic strengths lead to a lower solubility of struvite.

For practical purposes, the P-elimination efficiency also depends on the particle elimination process and therefore on particle size. When measuring dissolved phosphate, good removal efficiencies are obtained. Yet, when producing many fine particles, not all precipitated phosphorus can be easily separated from the liquid by sedimentation or filtration (Wilsenach *et al.*, 2007). Larger particles are

easier to separate, which will increase the overall P-elimination performance and above all the recovery potential.

5.5 Conclusions

Struvite formation from hydrolysed urine starts with fast spontaneous nucleation. The nuclei develop into crystals, to an average size between 36 (Experiment 1) and 136 μm (Experiment 15). Particles present in hydrolysed urine (in the range of 1.6 - 1.95 μm) do not affect the particle size distribution. Factors that do have an influence on average crystal size are the ones which affect supersaturation: higher supersaturation, either by weak mixing, pH towards minimal solubility or low temperature, leads to smaller particle sizes. Struvite precipitation from urine in a simple continuously operated CSTR is well possible, with a dissolved phosphate removal efficiency of >98%. No pH control is required. When considering scaling up, the scaling that occurs on the wall of the reactor may become an issue.

Under the conditions typically found in hydrolysed urine, larger crystals cannot easily be formed, leading to rather limited crystal sizes typical for struvite precipitation in urine (36 - 136 μm). Due to the negative effects for maximum phosphorus removal and recovery, dilution of urine should be avoided.

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Discussion and Outlook

The previous chapters have supplied many details about the technical and chemical aspects of struvite precipitation from source separated urine. This concluding chapter deals with its societal implementation, and the integration into the technical environment. More specifically, possible process trains for urine collection, storage and treatment will be discussed, followed by economical aspects.

6.1 Process train design

Struvite precipitation in this thesis was investigated as an important aspect of a urine separation scenario. Urine separation is considered as a potential innovation and “flexibilisation” of the current conventional wastewater system. Primarily, the technology requires a toilet specially designed for the separate collection of urine and/or waterless urinals, a urine storage tank in or near the household, one or more treatment units located either locally or centrally that processes the urine, and a means for transporting the urine from the storage tanks to the treatment unit. For each implementation project, choices have to be made regarding types of treatment units, as well as their order and their location. In this paragraph, a discussion is given on which factors are of influence on this discussion from the point of view of struvite.

6.1.1 Essential removal processes

Within this thesis, struvite precipitation is presented as a process to remove and recover phosphorus from urine. As a phosphorus removal method, struvite precipitation is very effective in terms of removal percentage (>99%). Yet, with the influent concentration being high as it is, still 2.1 ± 1.0 STD mgP.L^{-1} remains in the effluent (Figure 5-8). The EC Urban Waste Water Treatment Directive (UWWTD, 1991) gives guidelines for mixed wastewater treatment (97/271/EC, Table 6-1). Urine and wastewater are hardly the same, yet since the guidelines are in place to protect sensitive water bodies, we can use these values as an indicator for removal requirements for urine. The requirements will become more strict from 2015, putting into place also ecological requirements.

Table 6-1: Requirements for phosphorus and nitrogen removal from wastewater according to the EC Urban Waste Water Treatment Directive (UWWTD, 1991)

Parameter	Population equivalent	Concentration mg.L^{-1}	Minimum reduction %
Total phosphorus	10 000–100 000	2	80
	>100 000	1	80
Total nitrogen	10 000–100 000	15	70-80
	>100 000	10	70-80

As can be seen from Table 6-1, we not only need to provide sufficient phosphorus removal, also nitrogen removal must be guaranteed. Additionally, a safe discard of the urine waste stream requires COD and micropollutant removal. Currently, no guidelines are in place for micropollutants. Yet, their status of emerging compounds and the concern about their damage to particularly aquatic fauna certainly justify the inclusion of a micropollutant removal step within a process train. In fact, the possibility of removing micropollutants from urine being a concentrated small side stream is considered one of the major benefits of urine separation (Larsen *et al.*, 2004).

6.1.1.1 Nitrogen removal and recovery from urine

Nitrogen is present in large quantities in urine. One possible nitrogen conversion process for urine is nitrification (Johansson and Hellström, 1999; Udert *et al.*, 2003b; Oosterhuis, 2007). Yet, due to a lack of extra buffer capacity, only half of the ammonium will be nitrified in conventional biofilm and activated sludge reactors. The pH decrease due to nitrification inhibits advanced conversion (Udert *et al.*, 2003b). As a consequence, nitrification of urine results in an ammonium-nitrate or ammonium-nitrite solution with an approximate 1:1 composition. The ammonium-nitrite solution can be treated in a membrane aerated biofilm reactor, in which a combined process of nitrification and chemical nitrite oxidation takes place (Udert *et al.*, 2005). In these experiments, however, pH values as low as 2.6 were obtained. Ammonium nitrate is a popular fertiliser product; treatment could stop after this combined process. Alternatively, complete N removal can be achieved through the Anammox process (Udert *et al.*, 2003b).

Because nitrogen is no finite resource like phosphorus, removal rather than recovery processes have been the subject of research. Still, nitrogen recovery remains a possibility, as long as the energy balance comes out in favour of recovery. Several alternative systems for nitrogen recovery have been studied. Lind *et al.* (2000) were able to recover 65-80% of ammonia from urine through adsorption to natural zeolites, after a struvite precipitation step to remove the phosphorus. The combination of struvite with the zeolites also proved to be beneficial in agriculture. Freeze-thawing is a method proven to be applicable to urine, and this can lead to the concentration of 80% of all nutrients in 25% of the original volume (Lind *et al.*, 2001). The production of isobutylaldehydediurea from fresh urine was not very successful (Behrendt *et al.*, 2001, as cited in Maurer *et al.*, 2006). However, removal through stripping was shown to lead to a 97% removal rate of ammonium, which was recovered in the form of ammonium sulphate (Başakçılardan-Kabakci *et al.*, 2007).

The final method for nitrogen removal discussed here is tried both with urine (Kabdaşlı *et al.*, 2006) and other nitrogen and phosphorus rich streams (Uludag-Demirer and Othman, 2009; Zhang *et al.*, 2009): precipitation of struvite by adding magnesium and phosphate. Assuming urine with a nitrogen content of 8000 mg.L^{-1} , 0.57 mol.L^{-1} phosphorus needs to be added, e.g. in the form of 56 mg.L^{-1} of H_3PO_4 . To make this a sustainable alternative, phosphorus which was already earmarked for fertiliser production has to be applied. Optimising logistics would be the next challenge in this case.

Concluding, several techniques are available for (partial) nitrogen removal and recovery. Nitrogen removal following struvite precipitation is comparable to nitrogen removal from hydrolysed urine directly, except for the low phosphorus concentration, which may cause problems in a biological process.

6.1.1.2 Organic compounds and micropollutants removal

The concentration of organic substances in urine is high; the main contributor is urea. For the total of about $10000 \text{ g COD.m}^{-3}$ in fresh urine mainly organic acids, creatinine, amino acids and carbohydrates are responsible (Ciba Geigy, 1977 as cited by Udert *et al.*, 2006). 85% of COD in urine are easily biodegradable (Udert *et al.*, 2003b). Both aerobic and anaerobic degradation is possible. Udert *et al.* (2003b) found a substantial concentration of bacteria and organics in a viscous mass at the bottom of the collection tank, which they called urine sludge. A COD content of $0.18 \text{ g COD.gTSS}^{-1}$ was measured in this sludge. Anaerobic degradation processes take place, and in the presence of oxygen also aerobic degradation and even nitrification was observed (Udert *et al.*, 2006). However,

the high concentrations of COD also after storage (Udert *et al.*, 2003b; Ronteltap *et al.*, 2003) indicate that spontaneous degradation is not substantially removing COD from urine. Very little is mentioned about COD removal from urine in literature; for many of the streams used for experimental work, final COD removal is achieved in the conventional wastewater treatment plant. Yet, if we want to design a system separated from any wastewater treatment plant, COD removal should also be addressed. This can also be done by anaerobic treatment.

An important group of organic pollutants form the micropollutants. The term micropollutants is a collective name for organic compounds that occur in small concentrations. In our context, the term is primarily used for pharmaceutical residues and hormones. Despite their low concentrations, their effect can be substantial particularly on aquatic organisms: hormones and pharmaceuticals are designed to be highly effective in small doses. The removal of micropollutants from urine has been the topic of an increasing numbers of researchers. In general, a distinction must be made between processes that eliminate the micropollutants, and those that separate the micropollutants from the nutrients. The separation of nutrients and micropollutants is relevant to the production of a urine-based fertiliser, whereas the micropollutants must be eliminated for water-pollution control (Maurer *et al.*, 2006). Separation processes are primarily based on membranes or precipitation whereas removal processes are based on oxidation or adsorption (Larsen *et al.*, 2004). Well researched removal techniques are electrodialysis (Pronk *et al.*, 2006a; Zhang Y *et al.*, 2009) and nanofiltration (Pronk *et al.*, 2006b).

The removal of COD will not strongly affect struvite precipitation, the effect will be through the contributors to the ionic strength and those organic compounds that have an effect on the pH value (volatile fatty acids).

6.1.2 Different scenarios for collection and treatment of source separated urine

Borsuk *et al.* (2008) made different scenarios for implementation of urine separation in a new development project in Switzerland. Their study presented a selection of most attractive and interesting options: a status quo alternative, five peak shaving alternatives, and two nutrient recycling alternatives for the full catchment (Figure 6-1). The peak shaving alternatives comprise urine separating toilets in the households, which will each be connected to a small storage tank located in the bathrooms. No local treatment is foreseen; instead, the urine will be transported to the wastewater treatment plant via existing sewer lines using timers or controllers. This will give the operators an extra degree of freedom to handle the typical daily peaks better. Moreover, with a sophisticated steering mechanism, urine spills during combined sewer overflows can be minimized: during or shortly after rain events, the urine tanks will not be emptied. Another alternative was designed with separate piping for urine leading to an intermediate local storage tank. Transportation to the treatment plant would be accommodated with trucks. The third group of options includes nutrient recovery. This can be done either at the WWTP or onsite, by making use of small treatment units designed to process the urine of one or two multifamily buildings.

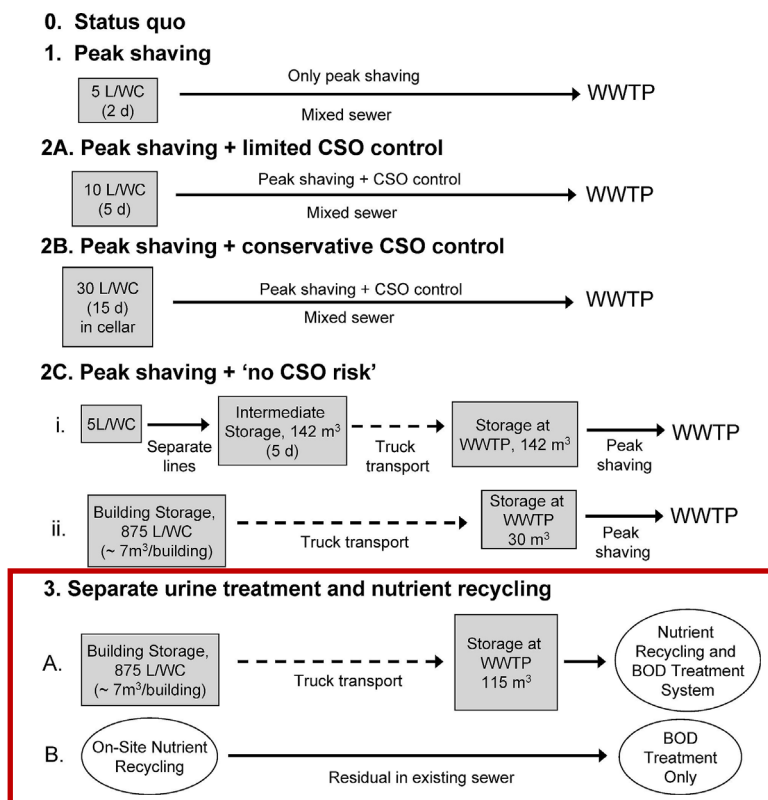


Figure 6-1: Schematic overview of the alternative scenarios as created by Borsuk *et al.*, 2008. For this work the focus lies within the red cadre.

Based on the results of this thesis, some technological support can be given in the decision making process on the nutrient recovery processes and their sequence. In the scheme of Borsuk *et al.* (2008), no differentiation is made between phosphorus and nitrogen recovery. Since in most cases these are different process steps, a differentiation will be made here. The order of processes can be flexible; yet, one decision in the process train does have consequences for the rest. For example, if partial biological nitrogen removal is chosen as a first option, subsequent phosphorus removal will have to deal with an altered composition of the urine solution.

6.1.2.1 Struvite precipitation followed by nitrogen removal

If the process is designed so that struvite precipitation takes place before nitrogen removal, the still elevated pH value is an advantage. The knowledge presented in this thesis regarding struvite precipitation at elevated pH, high buffer capacity, high ammonium concentration and high ionic strength can be applied. The almost complete removal of phosphorus (struvite precipitation removes only 2% of the ammonium, yet 99% of phosphorus) will however complicate biological processes arranged after struvite precipitation. If the process is designed to take place on the wastewater treatment plant, biological processes can make use of the nutrients from other wastewater streams. Several schemes have been suggested to integrate other streams with urine for struvite precipitation on the wastewater treatment plant; an example is given in Figure 6-2.

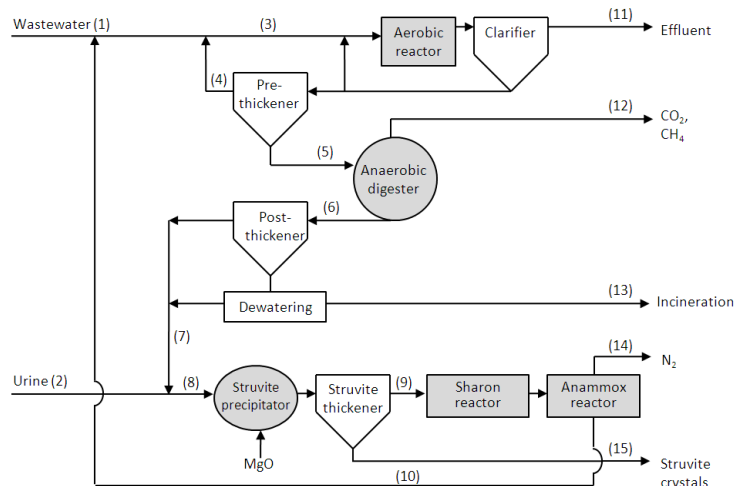


Figure 6-2: Proposed process flow diagram to treat wastewater and separately collected urine in one process, the so-called IntWUT (Integrated Wastewater and Urine Treatment; Wilsenach, 2006)

An alternative within this scheme would be to recover phosphorus on location, after which the stream is transported to the treatment plant. A set-up like this was suggested as the “Struvinoir”, a urine diverting toilet with a precipitation unit within the toilet (interview with professor Schuiling in Trouw, 1999). This kind of system would however require some buffer capacity: when leaving the body, urine contains hardly any ammonia and has a low pH. The urea hydrolysis process has to be given a day before subsequent phosphorus precipitation can be carried out optimally (Udert *et al.*, 2003a), meaning that for a four person household, a storage tank of at least 6 litres needs to be installed.

6.1.2.2 Nitrogen removal followed by struvite precipitation

Nitrogen removal can also be chosen as the first process within the treatment train. A good removal option would be one of the biological processes investigated by Udert *et al.* (2003). The systems comprised a moving-bed biological reactor (MBBR), a sequencing batch reactor (SBR) and a continuously stirred reactor (CSTR). The MBBR system produces ammonium nitrate as a final product, while the other two systems produced stable ammonium nitrite. Table 6-2 shows the influent and effluent concentrations of the 3 different systems.

Table 6-2: Data on nitrification performance in an MBBR, CSTR and SBR fed with hydrolysed urine (adapted from Udert *et al.*, 2003).

Reactor		MBBR	SD	CSTR	SD	SBR	SD
Influent ammonia	$gN.m^{-3}$	7100	100	7300	250	2240	100
Influent ammonia load	$gN.m^{-3}.d^{-1}$	750	50	1580	30	560	30
Reactor temperature	$^{\circ}C$	25.3	0.5	30	0.4	24.5	0.5
Effluent ammonia	$gN.m^{-3}$	3750	20	3880	110	1100	100
Effluent nitrite	$gN.m^{-3}$	75	2	3930	130	1180	50
Effluent nitrate	$gN.m^{-3}$	3730	60	60	30	30	2
Effluent pH	$gN.m^{-3}$	6.3	0.05	6.9	0.05	6.1	0.05

The implementation of an MBBR process would lead to an influent for the struvite reactor consisting of an ammonium-nitrate solution with a pH of 6.3 (Table 6-2). Effluent ammonia is still sufficient to remove all phosphorus; yet, pH adjustment is essential for optimal phosphorus recovery (>pH 8). The same would be valid for precipitating struvite in the effluent of an SBR or CSTR process. Since the buffer capacity of urine is strongly reduced due to the nitrification process (no bicarbonate left),

raising pH is easier within this composition. Yet, it will require more operation and chemical dosing, which limits the applicability of the systems for households.

An alternative to remove nitrogen from urine is to biologically nitrify ammonia to nitrate on location, and to dose the biologically produced nitrate to the sewer system. Nitrate dosing is frequently applied to serve as an electron acceptor in sewers to protect the sewers, and to prevent hydrogen sulphide production. Local biological nitrate production can help save on transportation and chemical delivery cost and effort. It requires aeration, but if the urine was transported to the wastewater treatment plant, it would have required the same amount of oxygen there. This system is successfully applied in one of the Dutch water boards: a project was initiated to locally nitrify separately collected urine in a small (2.5m³) reactor (Oosterhuis, 2007). The nitrate from urine fully replaces the commercial nitrate.

Struvite precipitation as a phosphorus recovery process can very well be implemented on a local scale, e.g. a reactor in the basement of an apartment building. If struvite precipitation is to be applied as a nitrogen removal process as well, also phosphorus has to be added in an optimal dosing. This is likely to be impractical for household systems. Full nitrification is a possibility for local treatment, if the nitrate can be used for odour reduction in the sewer. Yet, this will be a local system rather than a household application. With the current technology, a full nutrient removal installation for urine only is not yet recommendable for households, due to the operational demands.

6.2 Phosphorus recovery potential

We have shown that struvite precipitation can be an effective and straightforward way to recover phosphorus from source separated urine. Yet, in this thesis we have worked with hydrolysed urine, some artificial but mainly real. It is known that the phosphorus concentration in stored urine is lower than in fresh, due to spontaneous precipitation of phosphate minerals. With most current systems, the spontaneous precipitation of phosphorus reduces the amount available for P recovery with controlled struvite precipitation. As was shown in detail by Udert *et al.* (2003a, 2003b) precipitation of phosphate minerals starts to take place as soon as the hydrolysis process has set in. This process will continue until equilibrium is reached, or until one of the precipitants is no longer available, typically magnesium and calcium.

Udert *et al.* (2003a) present a table showing the phosphate, magnesium and calcium concentrations for 2 samples of fresh urine. Upon hydrolysis, pH will increase and all present magnesium and calcium will respectively form struvite and hydroxyapatite with phosphate ions. As a consequence, the dissolved phosphorus concentration will be reduced, equivalent to the molar magnesium and calcium concentration. The calculation of this process is shown in Table 6-3.

Table 6-3: Calculation of amount of phosphorus that remains in solution after ureolysis induced spontaneous precipitation. Data derived from Udert *et al.*, 2003a.

	Fresh Urine I		Fresh Urine II	
	mg.L ⁻¹	mM	mg.L ⁻¹	mM
PO ₄ -P	367	11.9	559	18.0
Mg	77	3.2	121	5.0
Ca	129	3.2	168	4.2
Precipitating as struvite	98.2	3.2	154.4	5.0
Precipitating as hydroxyapatite	46.9	1.9	61.1	2.5
Total removed by precipitation	204.4	5.1	300.4	7.5
Precipitated	55.7%		53.7%	
Remaining in solution	162.6		258.6	

For the values given in Udert *et al.* (2003a), the hydrolysis of urea will trigger spontaneous precipitation that leads to a reduction of more than 50% in the dissolved phosphate concentration.

Although in this thesis no fresh urine analyses were done, the phosphorus concentrations measured in the storage tank are well within the range of the calculated phosphorus concentrations after storage (e.g., Table 5-1: $241 \pm 15 \text{ mg P.L}^{-1}$).

The spontaneous precipitation process in the collection and transport system means a substantial reduction (>50%) of the phosphorus recovery potential from urine separating systems. The recovery efficiency could be improved if a system or device is put into place to enable recovery this spontaneously precipitated phosphorus. However, it can also be further reduced if the urine is brought into contact with more calcium and magnesium ions, typically present in tap flush water.

Not directly limiting for the phosphorus recovery potential but a negative aspect of stored urine collection in general is the substantial loss of ammonia in the urine collecting systems, which can be up to around 50% (GTZ, 2009). Because of environmental concerns, this should be avoided. This can be done by good engineering on the ventilation pipes (GTZ, 2009).

6.3 Costs of struvite precipitation

For calculation of the costs of struvite precipitation, several aspects play a role. An important aspect is the layout of the process. Local storage requires smaller tanks, yet in a larger quantity. Local treatment requires additional material, while in most scenarios transport cannot yet be fully excluded. Hence, this will be a more expensive scenario. If other costs can be avoided with the treatment, such as transporting nitrate to a pumping station to prevent odour formation, the balance will turn out more positive. Some money can possibly be saved when applying a magnesium by-product for struvite formation. Costs also differ substantially per country, due to the price differences in local materials. For comparison, a polyethylene tank of one cubic metre is estimated at €1.900,- in the Netherlands – this will be considerably cheaper in most developing countries.

Wilsenach (2006) made a preliminary cost evaluation of the implementation of urine separation technology. He came to an estimation of €2000 per "urine equivalent" (ue) per year for urine collection, nitrification-denitrification anammox and struvite precipitation. This is quite substantial. These costs may be reduced further once the process becomes more mainstream, and when struvite can be sold or at least applied as a fertiliser. Moreover, for new to develop scenarios, designers may look for integration options with existing technologies to reduce the total costs. Another aspect of cost saving comes from the side of the wastewater treatment plant. Wastewater without urine has much smaller hydraulic retention time requirements. This not only reduces the energy demand for treatment, it also increases the capacity of the plant in terms of connections. Wilsenach (2006) also showed that the resulting sludge is richer in organic matter and generates more than three times as much methane: separating 50 to 60 per cent of the urine could turn sewage works from energy consumers to producers, in the range of 2.5 watts per person. These considerations indicate that the discussion on the costs of struvite precipitation alone is not so interesting: rather, we need to observe the costs for the complete wastewater treatment process and how they change when urine separation is implemented.

6.4 Application potential of struvite as a fertiliser

In this work, we have shown that struvite precipitation from urine is very well possible, and details about the precipitation are given. Struvite formation was shown to be an effective phosphorus removal method which reduces the dissolved phosphorus from the wastewater stream urine with 99%. Yet, for the implementation of phosphorus recovery, the produced struvite needs to be brought back into the phosphorus utilizing industry. Since 80% of our mined phosphorus is used in fertiliser production, recycling the produced struvite as a fertiliser is a good option.

Struvite is a known fertiliser product. Its application is as an inorganic slow-release fertiliser: the release of nutrients depends on soil moisture, pH and temperature. Nutrients are released over a period of time, sometimes lasting up to 12 months. This means that fewer applications are needed than with regular directly available fertilisers. In addition, a slow release reduces the risk of nutrient leaching groundwater (Shaviv, 2003). However, crops for consumption are usually harvested within a few months. A careful calculation of the amount of fertiliser is needed to prevent the release of nutrients after harvesting. Moreover, the fixed ratio of N:P:Mg in struvite may not correspond to the requirements of all crops, leading to potential over-fertilising or nutrient limitations.

In the Netherlands, fertiliser application laws are strictly related to the type of crop that is grown. No more nitrogen and phosphorus may be applied than is necessary for the crop. For the application of animal manure, which has to be mineralised first before the organically-bound nutrients become available, application guidelines are drawn up per soil type and crop type. These guidelines are based on field studies and serve the purpose of preventing over-fertilisation. For struvite, similar guidelines could be drawn up. Currently, due to the excess of animal manure in the Netherlands, government policy stimulates the application of manure as a fertiliser over artificial fertiliser. For struvite from urine a similar stimulation construction is considered possible (Crijns, 2008). The reduced risk of heavy metal introduction through struvite compared to artificial, mined fertilisers will certainly be of help in this respect.

Figure 6-3 shows the contributions of the different types of fertilisers applied in the Netherlands in $\text{kg} \cdot \text{ha}^{-1}$ agricultural land. The market for struvite fertiliser would specifically be the amount of artificial fertiliser applied for phosphorus. Clemens (2008) compared the application of inorganic fertiliser in Western Europe (Germany 103, Austria 33, Netherlands 155, Sweden 79 and Europe 70 $\text{kg} \cdot \text{ha}^{-1}$) and concluded there is a substantial market for (natural) inorganic fertiliser.

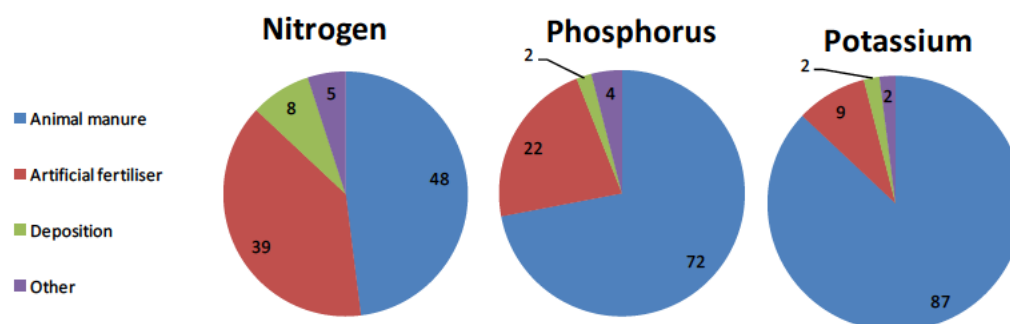


Figure 6-3: Types of fertiliser used in Dutch agriculture in 2008 (Centraal Bureau voor de Statistiek, 2009)

Swiss studies show that consumers are willing to buy products produced with fertilisers from human urine (Pahl-Wostl *et al.*, 2003). An additional option to reuse struvite in agriculture would be in the

production of goods that are processed before human consumption, like olives for olive oil, or not consumed at all, such as flowers and other horticultural products. Also the worldwide increase in biofuel production may profit from this man-made fertiliser product. Already, willow production as a source of biofuel takes place on an increasing scale, with wastewater as a main energy and nutrient source (Hasselgren, 1998). Since struvite contains significantly less heavy metals and endocrine disruptors than sewage (Chapter 4), struvite can be used for biofuel production in areas more sensitive to groundwater pollution.

6.5 Other streams in wastewater management that can be used for struvite formation

There are many publications on struvite precipitation, either to describe the problem of scaling, or to emphasize the potential of struvite as a recovery product. However, many of these publications focus on streams within the biological wastewater treatment, preferably near the sludge production and management line. The streams are comparable on many points: a small but highly concentrated side stream, high in nitrogen and phosphorus (depending on the type of stream). Yet, there are also some difference, of which pH is potentially the most important one. Almost all publications refer to pH adjustment of some sort in order to get their system into the pH range optimal for struvite precipitation. For urine, this is not necessary: the hydrolysis process of urea automatically brings the pH up. Not having to raise the pH is of great economical benefit. Yet, it also means we cannot control the crystallisation process other than by adding magnesium.

Another difference may be the ionic strength and composition of the solution. The presence and abundance of other ions are of consequence for the solubility of struvite (Chapter 3), and therefore on the level of supersaturation. Table 6-4 gives an overview of several researchers reporting on struvite precipitation in other wastewater streams. Magnesium chloride is a favourite precipitant, and generally high removal efficiencies are found. A number of researches looked at struvite precipitation for ammonia recovery, by adding a phosphate sources. With almost all other waste streams the pH needs to be adjusted in order to come to good removal results. Overall, it can be concluded that struvite precipitation works well in several wastewater streams.

Table 6-4: Overview of other waste or process water streams which have been applied for struvite formation.

Wastewater stream	P (mg.L ⁻¹)	N (mg.L ⁻¹)	pH (-)	Type of magnesium	Mg:P (-)	P removal efficiency (%)	Ref.
Landfill Leachate	Added to remove NH ₄ -N	2520 (± 100)	8.1→9.5	MgCl ₂	1.15	85 for N	Zhang <i>et al.</i> , 2009
UASB Effluent	370 (±30)	1318 (±70)	7.95 (±0.10)	MgCl ₂ + KH ₂ PO ₄ MgSO ₄ MgO	1 1	84 for N <84	Yetilmezsoy and Sapci-Zengin, 2009
Anaerobic lagoon water	50.5	142	7.5→9	MgCl ₂	1.2 1.6	85 91	Nelson <i>et al.</i> , 2003
Filtrate from sludge Dewatering	100-110	n.m.	→8.8	Mg(OH) ₂	1	90	Ueno and Fujii, 2001
Anaerobic digester supernatant	24 (±5)	1400 (±2.5)	8.5	MgCl ₂	1	92	Türker and Celen, 2007
Hydrolysed Urine	223 (±34)	5245 (±759)	9.0	MgCl ₂	1.5	99	This Work

6.6 Conclusion

This thesis has shown that struvite precipitation is an excellent way to not only remove but also recover phosphorus from source separated urine. The thermodynamics of the struvite precipitation process are shown, and more insight is obtained in what role other components play in this process, not only due to their concentrations and hence effect on ionic strength but also via their bindings to the struvite components. With respect to micropollutants, struvite from urine can safely be applied as a fertiliser, since the bulk of micropollutants remain in solution rather than be incorporated into the crystal lattice. For some heavy metals, this risk is somewhat higher, and care should be taken in order to prevent the stored urine from obtaining elevated heavy metal concentrations. This can be done by avoiding any metals in the urine collection system. Should there be any unavoidable elevated heavy metal concentrations, then it is advisable to dispose of the precipitates at the bottom of the urine storage tanks, since many of the metals precipitate in here in the form of metal carbonate or hydroxide.

For practical applications, the knowledge on struvite precipitation systems is improved. The effects of a number of parameters on crystal size and phosphorus recovery efficiency have been revealed, and were shown to be mainly related to the degree of supersaturation. Practitioners can use the given practical values for the conditional solubility product, and the method given to obtain an estimation of the dilution factor and ionic strength based on conductivity measurements. This can be applied while working in the field of struvite precipitation in hydrolysed urine as well as for solutions comparable to urine with respect to ionic composition and ionic strength.

6.7 Outlook

There is a collective notion that we can and should make our current wastewater treatment system more sustainable, and there is a willingness to act. This thesis has contributed to the knowledge on how phosphorus recovery through struvite formation from urine can be a part of this. More and more projects are starting up around urine separation, both in industrialised and developing countries. Different schemes for local decentralised treatment oriented towards reuse and recovery of energy and nutrients are being designed and implemented. In these designs, struvite precipitation is gradually seen as a standard step to remove and recover phosphorus. Also in schemes without urine separation but with concentrated wastewater, like the decentralised vacuum system with onsite anaerobic treatment (Meulman, 2008), struvite precipitation can play an important role.

Urine separation technology is ready to be a part of new sanitation technology. Naturally, not all existing toilets will be replaced by (waterless) urine separation toilets. This would be too costly and unsustainable. Yet, in new areas where it makes technically and environmentally sense to install them, they should be considered seriously. For arid areas, for example Australia or the dry parts of the United States, a sanitary system not wasting any precious drinking water should be warmly welcomed. For areas where getting connected to the existing sewer system and consecutive wastewater treatment plant is very expensive, local solutions are designed. A good example are the outskirts of Berlin, where several small settlements are not connected to a sewer system. Different decentralised systems are employed to treat the wastewater of these households. At one location, a membrane bioreactor system treats the wastewater of about 200 inhabitants (ENREM, 2009). A remarkably high nitrogen removal is achieved. However, phosphorus removal lacks behind,

particularly in the low-tech part of the MBR system. For this kind of situation, urine separation within the households can offer a good alternative. The toilets would enable phosphorus removal by struvite precipitation; the effluent of the precipitation step can be treated in the MBR system while good results for phosphorus in the effluent are obtained.

Future research in struvite precipitation from urine

What stays a bottleneck in urine separation technology is the issue of unwanted precipitation in the urine collection system. Precipitation in inconvenient locations within the urine collection system can lead to blockages. We know that upon excretion, urine has a pH of 6 and hardly any precipitation can take place. After coming into contact with urease - an omnipresent enzyme excreted by bacteria - urea is hydrolysed, pH rises and precipitation sets in. This process takes place already during transport in the urine collection system - the numerous reporting of pipe blockages testify of that. One of issues that remains unsolved is how and where this precipitation process takes place in detail. A good indication could be given by measuring the pH or conductivity over transportation system. As soon as urea hydrolysis sets in, both will increase. Obtaining more knowledge on the hydrolysis process in the transportation system will help preventing problems. Details about diameters, connections and bends in relation to precipitation potential will allow pre-calculations and minimisation of precipitation risks beforehand. This can be used for system modelling. A study is currently being undertaken by PVC pipe producer Dyka and Windesheim technical college in Zwolle, the Netherlands. Once the precipitation potential of different sewer parts is known, a module can be set up to determine the layout with minimal precipitation potential.

Another future research activity involves modelling of the crystallisation process. Some work in this area has been done at University of British Columbia (Rahaman *et al.*, 2008) and in Brisbane, Australia (Imtiaj Ali and Schneider, 2008). A model suitable for nucleation and crystal growth in an ideal situation and in urine would be beneficial for estimating the factors with the biggest impact on precipitation and crystal size development. The results from this work with crystal sizes in different systems can serve as a base for such a model.

And finally, to the author's knowledge, no detailed research has been conducted on the different magnesium sources that can be applied for struvite precipitation. The behaviour of the different magnesium sources and availability for reaction in urine is an important factor for optimal struvite precipitation.

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Appendix I

Thermodynamics of Struvite Precipitation in Source Separated Urine

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Abstract

The thermodynamics of struvite (MgNH_4PO_4) precipitation in source separated and artificial urine under controlled addition of magnesium chloride (MgCl_2), magnesium oxide (MgO) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) were investigated. The solubility product of struvite in source separated and artificial urine was identified by use of experimental results in a precipitation potential model designed for working with urine. A conditional solubility product of $10^{-11.7 \pm 0.51}$ was determined, which can be used for solutions comparable to source separated urine. With the precipitation model the inorganic complexes MgPO_4^- , MgHPO_4 , $\text{NH}_4\text{HPO}_4^-$, NaHPO_4^- , MgSO_4 , MgHCO_3^+ , MgCO_3 , and NH_4SO_4^- were determined as significant in urine and they exert influence on the solubility of struvite. Ionic strength and formation of dissolved complexes were considered in calculating the average value of the standard solubility product of struvite in urine, which is $10^{-13.41 \pm 0.31}$. This value is slightly smaller but agrees well with the solubility products reported recently in the literature.

Organic complexing agents do not influence the solubility of struvite.

Keywords

struvite, solubility product, precipitation thermodynamics, source separated urine

Introduction

Forced struvite (MgNH_4PO_4) precipitation has been recognised as a way to recover phosphate from liquid waste. Several pathways have been described, mostly focusing on the formation of struvite from digester supernatant (Wild *et al.*, 1996, Battistoni *et al.*, 1997, Booker *et al.*, 1999), animal waste slurries (Schuiling and Andrade, 1999, Burns, R. T. *et al.*, 2001) or directly out of wastewater (Durrant *et al.*, 1999, Webb and Ho, 2001). Using struvite precipitation to recover phosphorus from urine has the potential to capture up to 50% of the P-flux in the urban wastewater stream.

Struvite is an orthorhombic crystal consisting of ammonium, magnesium and phosphate in a molar ratio of 1:1:1. Struvite precipitation is controlled by pH, the degree of supersaturation, temperature and the presence of other ions in solution (Doyle and Parsons, 2002). Supersaturation is reached when the activity product (IAP) exceeds the solubility constant (K_s) of a solid:

$$\text{Degree of saturation} = \frac{IAP}{K_s} \quad (\text{House, 1999})$$

Fresh urine contains 0.27 ± 0.05 M urea, only little ammonia and has a pH of approximately 6.2 (Ciba-Geigy, 1977). Under the influence of bacterial urease, complete hydrolysis of urea takes place, ammonia is formed and the pH increases to above 9 (Udert, 2003a), thereby favouring the chemical properties of source separated urine for the precipitation of phosphorus compounds. The complexity of the solution makes the understanding of the underlying thermodynamics and kinetics difficult.

Many details on the thermodynamics of struvite precipitation in aqueous solutions are known, (Aage *et al.*, 1997, Battistoni *et al.*, 1997, Doyle and Parsons, 2002, Jaffer *et al.*, 2002) but considerably less on the kinetics (Bouropoulos and Koutsoukos, 2000) and precipitation in high strength liquors (Babic-Ivancic *et al.*, 2002). Both parts are important in struvite precipitation research.

Objectives

This research was conducted to investigate the thermodynamics of struvite precipitation in source separated and artificial urine under controlled addition of magnesium chloride (MgCl₂), magnesium oxide (MgO) and magnesium hydroxide (Mg(OH)₂).

Background

Solubility product

The solubility product (K_{so} , or often expressed as the $pK_{so} = -\log(K_{so})$) is calculated from the total molar activity of the free lattice ions in solution at solid-solute phase equilibrium. In high concentrated solutions such as seawater, apparent or conditional equilibrium constants (K_s or $pK_s = -\log(K_s)$) are frequently used because calculating the ion activity would be too sumptuous or even impossible. The conditional solubility product K_s can only be applied for the kind of solutions they were estimated for and is defined as:

$$K_s = [Mg^{2+}] \cdot [NH_4^+] \cdot [PO_4^{3-}]$$

where $[Mg^{2+}]$ is the measured dissolved concentration of magnesium and $[NH_4^+]$ and $[PO_4^{3-}]$ are derived from the measured concentration of the sum of ammonia and ammonium $[NH_4^+ + NH_3]$ and dissolved phosphate $[P]$, respectively:

$$[NH_4^+] = \frac{[NH_4^+ + NH_3]}{(1 + 10^{pH - pK1})} \quad [PO_4^{3-}] = \frac{[P]}{(1 + 10^{pK2 + pK3 - 2pH} + 10^{pK3 - pH})}$$

where $pK1 = 9.24$, $pK2 = 7.21$ and $pK3 = 12.36$ according to the equilibrium constants in Table A-1.

Table A-1: Standard solubility product of struvite as reported in literature

pK_{so}	Temp. [°C]	Speciation	Ionic Strength	Reference
9.4	nm	no	mention of strong pH effect	(Borgerding, 1972)
12.36	25	yes	0	(Buchanan <i>et al.</i> , 1994)
12.6	25	no	negligible	(Bube, 1910)
12.94	25		0	
12.22		yes	0.07	(Aage <i>et al.</i> , 1997)
13.12	25			
12.97	35	yes	nm	(Burns and Finlayson, 1982)
13.15	25	yes	0	(Taylor <i>et al.</i> , 1963)
13.26	25	yes	nm	(Ohlinger <i>et al.</i> , 1998)
13.36	25			
13.27	37	yes	0.5	(Babic-Ivancic <i>et al.</i> , 2002)
n.m not mentioned				

Many researchers report on the value of the solubility product of struvite, with pK_{so} values ranging from 12.22 to 13.36 (Table A-1). A pK_{so} value of 12.6 was first reported by Bube in 1910, which was obtained at 25° C and negligible ionic strength. This value is commonly used in water chemistry texts today (Snoeyink and Jenkins, 1980, Stumm and Morgan, 1996), although no calculation on the speciation was taken into account. In 1963, Taylor *et al.* reported a value of 13.15, calculated with an ionic strength obtained with the Güntelberg approximation to the Debye-Hückel equation. Burns and Finlayson (1982) obtained a solubility product of 13.12 by using the Davies approximation:

$$-\log f_i = 0.5z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (\text{Stumm and Morgan, 1996})$$

For solutions of high ionic strength the Davies approximation is used, although it is also limited to an ionic strength of $\leq 0.5\text{M}$. Most authors state that the Davies approximation should only be applied for $I \leq 0.1\text{ M}$ (Pitzer, 1979), but the variance of the equilibrium constants and other data is so high that the error introduced by using the Davies approximation is negligible.

Complexation

The fundamental problem of calculating the ion activity product of struvite is the amount of magnesium, ammonium and phosphate that are effectively available for struvite precipitation. The species can be involved in other complexing equilibria. Also, the speciation of the components is strongly dependent on pH and ionic strength. Ionic strength and complex formation both have an increasing effect on the solubility product. At higher ionic strength the electrostatic interactions of ions are increased, thereby reducing the ion activity and increasing the solubility. In struvite precipitation, complex formation primarily affects the availability of magnesium and phosphate ions.

The need for speciation and complex formation is indicated many times in literature. Although Stumm and Morgan (1996) do not make any calculations on speciation for determining the solubility product of struvite, they do mention that other equilibria beside the solubility equilibrium occur in a solution, and the side reactions increase the solubility. Ohlinger *et al.* (1998) state that accurate determination of struvite solubility requires consideration of ionic strength effects and inclusion of magnesium and phosphate complexes in the analysis, while both factors increase solubility. In literature, many different complexes involving one or more of the struvite species are mentioned. Ohlinger *et al.* (1998) take only MgHPO_4 into account while other complexes were expected to have little effect on the pK_{so} value in the pH range of 6.3-8.1. Buchanan *et al.* (1994) include 3 different magnesium ammonium complexes as well as magnesium hydroxide formation. Bouropoulos *et al.* (2000) also involve magnesium ammonia complexes.

Calculations

Within this work, complexation as well as ionic strength is considered for determination of the solubility product. A selection was made on the complexation reactions within source separated urine. The most dominant species ($>3\%$ of the struvite components Mg , PO_4 and NH_4 in equilibrium) were selected using a model for predicting the precipitation potential in urine, developed by Udert *et al.* (2003b). This model includes many kinetic data on chemical reactions involved in source separated urine. The equilibria constants are taken from literature. (Viellard and Tardy, 1984, Stumm and Morgan, 1996, Martell *et al.*, 1997) When necessary, literature data were adjusted to $T=25^\circ\text{C}$ and to the ionic strength with the Van 't Hoff equation and the Davies approximation, respectively (Udert *et al.*, 2003b). All complexes considered are pH dependent and influence each other, therefore the equilibrium concentrations and ionic strength are determined by iteration.

Activity factors and ionic strength were determined with the Davies approximation to the Debye-Hückel equation, taking into account all ion species present in source separated urine defined in the model. Ionic strength was calculated with:

$$I = 0.5 \sum_i c_i \cdot z_i^2 \quad (\text{Stumm and Morgan, 1996})$$

Table A-2: Dissolved complexes considered for the determination of the solubility product of struvite in source separated urine. The values for the equilibrium constants are given for 25 °C and an ionic strength of 0. When necessary, literature data taken from Martell *et al.* (1997), Stumm and Morgan (1996) and Viellard and Tardy (1984) were adjusted with the Davis approximation.

Equilibrium						pK _{so}
Mg ²⁺	+	H ₂ PO ₄ ⁻	↔	MgPO ₄ ⁻	+ 2H ⁺	12.96
Mg ²⁺	+	H ₂ PO ₄ ⁻	↔	MgHPO ₄	+ H ⁺	4.3
		H ₂ PO ₄ ⁻	↔	HPO ₄ ²⁻	+ H ⁺	7.21
		HPO ₄ ²⁻	↔	PO ₄ ³⁻	+ H ⁺	12.36
NH ₄ ⁺	+	HPO ₄ ²⁻	↔	NH ₄ HPO ₄ ⁻		-1.3
Na ⁺	+	H ₂ PO ₄ ⁻	↔	NaHPO ₄ ⁻	+ H ⁺	6.01
Mg ²⁺	+	SO ₄ ²⁻	↔	MgSO ₄		-2.37
Mg ²⁺	+	HCO ₃ ⁻	↔	MgHCO ₃ ⁺		-1.07
Mg ²⁺	+	HCO ₃ ⁻	↔	MgCO ₃	+ H ⁺	7.35
		HCO ₃ ⁻	↔	CO ₃ ²⁻	+ H ⁺	10.33
		NH ₄ ⁺	↔	NH ₃	+ H ⁺	9.24
NH ₄ ⁺	+	SO ₄ ²⁻	↔	NH ₄ SO ₄ ⁻		-1.03

Experimental set-up, material and methods

Experiments were conducted to investigate the precipitation thermodynamics of struvite in source separated and artificial urine under controlled addition of 3 magnesium sources. For these experiments, slightly diluted, completely hydrolysed source separated urine was collected from a urine collecting system (consisting of 3 waterless urinals and one NoMix toilet). Artificial urine was prepared according to the recipe of Udert *et al.* (2003c). This preparation does not contain any organic components, so complexation of struvite components with an organic complexing agent is excluded.

Table A-3: Composition of artificial urine in deionised water (Udert, 2003c).

Species	g.L ⁻¹	mM	Species	g.L ⁻¹	mM
Na ₂ SO ₄ water free	2.3	16.19	NaCl	3	51.33
KCl	3.4	45.61	NH ₄ HCO ₃	21	265.64
NH ₄ Cl	3.9	72.91			
NaH ₂ PO ₄	2.0	16.67	NH ₄ OH	17 mL.L ⁻¹	227.5

Samples were taken from a tap on the bottom of the 0.5 m³ collection tank (HRT urine >14 weeks), and from an extra tap on the end of the piping system right before the collection tank (HRT urine in the system < 1 week). The composition of the urine used for the experiments are compiled in Table A-4. The source separated urine was slightly diluted because of flushing water from the NoMix toilets. The dilution factor was calculated by comparing the total nitrogen measured to the standard nitrogen concentration of urine (8 gN.L⁻¹ urine, (Ciba-Geigy, 1977)). Batch tests were performed in glass volumetric flasks of 750 ml (real urine experiments) and 500 ml (artificial urine) which were stirred with magnetic stirrers and covered to prevent ammonia volatilisation. Magnesium oxide and magnesium hydroxide were added as a suspension, the water free magnesium precipitants all originated from MERCK (analytical quality). For analysis, 20 ml samples were taken and filtered through a Whatman GF/F filter (0.7µm), acidified with 1.5 ml 2M hydrochloric acid and stored at 4 °C until analysis. Total ammonia, given as the sum of ammonia + ammonium, and phosphate concentration were determined by Flow-Injection-Analyser (FIA, Ismatec AG), magnesium was measured with ICP and ortho-phosphate with IC. COD analyses were done with Dr. Lange LCK 014.

Table A-4: Composition of the dissolved components [mM] in urine used for the experiments. Legend: art = artificial urine (recipe see Table A-1).

Experiment	Storage time [wks]	COD [g.L ⁻¹]	Dilution factor	pH [-]	P	NH ₄ ⁺ +NH ₃	Na ⁺	Cl ⁻	K ⁺	CO ₂ + HCO ₃ ⁻	SO ₄ ²⁻	Mg concentration after addition	Mg source
A1	< 4	n.d.	1.77	9.00	8.72	232	80	73	37	176	11	8.45	MgCl ₂
B1	> 14	6.10	1.77	9.01	5.71	322	68	62	32	91	9	2.96	MgO
B2	< 1	5.42	1.87	9.12	5.13	307	64	59	30	82	9	3.00	
B3	art.	-	1.14	9.17	16.7	501	88	149	40	219	14	2.97	
C1	> 14	5.82	1.93	8.99	4.20	299	62	57	29	77	8	5.98	Mg(OH) ₂
C2	< 1	6.04	1.86	9.15	3.74	309	65	59	30	83	9	6.02	
C3	art.	-	1.14	9.09	16.7	501	88	149	40	219	14	5.99	

Results and discussion

The solubility product of struvite in source separated and artificial urine was identified (Table A-5). All calculations were done in Aquasim (Reichert 1994) with the precipitation potential model (Udert, 2003b).

Table A-5: The conditional (pK_s) and standard (pK_{so}) solubility product of struvite in urine

Experiment	Storage time urine [wks]	pK _s [-]	pK _{so} [-]	I [-]	T [° C]	pH [-]	P _{equil} [mM]	Mg _{equil} [mM]	mol Mg used per mol PO removed	Mg source
A1	< 4	12.41	13.55	0.34	22	9.02	0.50	0.22	0.97	MgCl ₂
B1	> 14	11.28	13.00	0.40	23	9.03	3.65	0.04	1.00	MgO
B2	< 1	11.68	13.49	0.40	22	9.13	0.97	0.04	1.00	
B3	artificial	11.17	13.31	0.52	22	9.13	9.78	0.02	0.94	
C1	>14	11.89	13.60	0.38	23	9.03	3.13	0.01	1.02	Mg(OH) ₂
C2	< 1	12.22	13.89	0.39	22	9.16	0.03	0.68	0.97	
C3	artificial	11.18	13.06	0.52	22	9.08	9.17	0.02	1.01	

The average value of the conditional solubility product for struvite and for slightly diluted urine can be calculated with $10^{-11.7 \pm 0.51}$. This means that compared with the solubility products in Table A-1 struvite is much more soluble in urine than in other solutions. E.g.: Using the solubility constant pK_s of 13.2 and neglecting the ionic strength, the concentrations of dissolved phosphorus and magnesium at the end of experiment A1 (Table A-5) would have been 0.28 mM and 0.005 mM, respectively. The real measured concentrations were with 0.5 mM dissolved phosphorus and 0.22 mM for magnesium significantly higher. Figure A-1 shows the correlation between the amount of added magnesium and the fraction of remaining phosphorus for experiment A1. Using an equimolar amount of magnesium chloride leads to a 96% elimination of dissolved phosphorus.

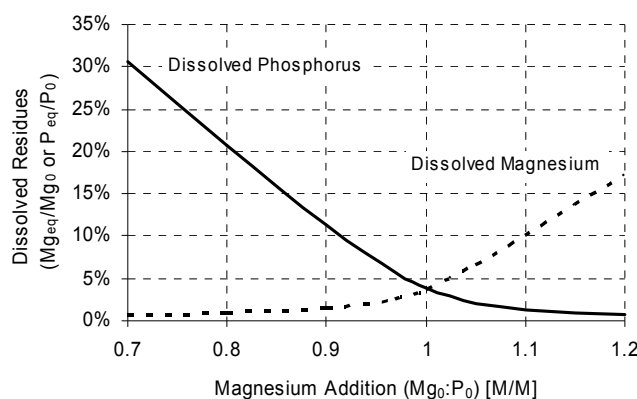


Figure A-1: The effect of magnesium addition on the dissolved phosphorus and magnesium concentration at equilibrium. The calculations were done with the urine composition of experiment A1. The initial magnesium is given as molar ratio of the dissolved phosphorus concentration. The residues are given as the percentage of dissolved and therefore not precipitated phosphorus or magnesium.

In order to compare the results from the experiments with the data given in the literature we considered the ionic strength and the formation of dissolved complexes (Table A-2). The average solubility product for struvite is given with $10^{-13.41 \pm 0.31}$. This value is slightly smaller but agrees well with the solubility products reported recently in the literature. The considered inorganic complexes MgPO_4^- , MgHPO_4 , $\text{NH}_4\text{HPO}_4^-$, NaHPO_4^- , MgSO_4 , MgHCO_3^+ , MgCO_3 , and NH_4SO_4^- play a significant role in urine and influence the solubility of struvite.

The fact that inorganic complexes alone are sufficient to explain the change in struvite solubility indicates that organic complexing agents do not influence the solubility of struvite. This statement is also backed up by the observation that the apparent solubility do not differ significantly between the different types of urine.

Table A-6: Calculated concentrations of the species used for the computation of pK_{so} (Table A-1), activity factors $f_1=0.70$, $f_2=0.24$, $f_3=0.04$ for all experiments.

Exp.	Mg^{2+} [μM]	NH_4^+ [mM]	PO_4^{3-} [μM]	MgPO_4^- [μM]	MgHPO_4 [μM]	$\text{NH}_4\text{HPO}_4^-$ [mM]	NaHPO_4^- [mM]	MgSO_4 [μM]	MgHCO_3^+ [μM]	MgCO_3 [μM]	NH_4SO_4^- [mM]
A1	91.9	157	0.54	3.15	1.02	0.17	0.10	15.3	2.78	74.8	4.72
B1	3.49	218	4.06	0.81	0.24	1.53	0.66	0.49	1.40	4.00	5.80
B2	15.5	192	1.28	1.16	0.66	0.34	0.17	2.32	5.77	20.8	5.34
B3	7.36	314	12.9	0.66	0.56	5.13	1.28	11.5	1.19	4.25	7.06
C1	4.08	202	3.33	0.79	0.24	1.21	0.57	0.60	1.52	4.26	5.55
C2	22.8	189	0.43	0.56	0.13	0.10	0.053	3.41	8.42	32.5	5.29
C3	3.86	327	10.1	2.00	0.53	4.69	1.35	0.44	2.27	7.23	7.21

Conclusions

In this paper, the thermodynamics of struvite precipitation in source separated and artificial urine have been studied. A conditional solubility product K_s of $10^{-11.7 \pm 0.51}$ was determined. This value considers the dependency of the solubility on the pH, but neglects the influence of the ionic strength and complexation reaction in the dissolved urine matrix. Due to these effects the solubility of struvite in urine is much higher than under conditions usually applied to determine solubility constants.

In order to compare the obtained conditional solubility product with the K_{so} values from literature we adjusted the measured concentrations to the ionic strength of urine with the Davis approximation and considered the following inorganic complexes: $MgPO_4^-$, $MgHPO_4$, $NH_4HPO_4^-$, $NaHPO_4^-$, $MgSO_4$, $MgHCO_3^+$, $MgCO_3$, and $NH_4SO_4^-$. This approach leads to a standard solubility product K_{so} for struvite of $10^{-13.41 \pm 0.31}$ as an average for all performed experiments, which does not significantly differ from the solubility products reported in the recent literature (Table A-1).

The inorganic complexes used for the estimation of the standard solubility product K_{so} were sufficient to explain the measured dissolved concentration of ammonia, magnesium and phosphate. In addition, no difference could be identified between precipitating struvite in source separated urine with organic compounds and inorganic artificial urine. This leads to the conclusion that in our experiments organic complexing agents do not influence the solubility of struvite significantly.

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Curriculum Vitae

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